

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1940.

Catalysts for synthesis of liquid hydrocarbons from carbon monoxide and hydrogen. VI, VII.
—See B., 1939, 1208.

Production of isobutane from normal butane.
—See B., 1939, 1209.

Catalytic oxidation of olefinic hydrocarbons.
—See B., 1939, 1208.

Relations of "oxygen and peroxide effect" and of hypochlorous acid addition to the structures of unsaturated organic compounds. A. MICHAEL (J. Org. Chem., 1939, 4, 519—530).—Designating the vibratory or co-vol. of an atom as a sphere, the primary phase of a chemical reaction, i.e., polymol. formation, may be represented by contact of these spheres and further reaction by segmentation increasing with the conversion of the free chemical into bound chemical energy. The "oxygen-peroxide" effect functions catalytically; in agreement, the first phase in the abnormal reaction may be conceived as a polymol. of O or peroxide at its oxygens and the saturated carbons of the substance. According to the principle of partition the polymol. formation of isobutene with the O₂ mol. may proceed in three directions: (1) by bilateral contact between the O and the unsaturated C atoms; (2) by unilateral union at the terminal unsaturated C (Winstein and Lucas, A., 1938, II, 224); and (3) at the intermediate, relatively positive, unsaturated C. Diagrams are given. The O in (1) should not noticeably alter the affinity relationships of the unsaturated C atoms for the components of HBr and, therefore, the course of the addition. In (2) the O accentuates the difference between the affinities of the unsaturated C for the components of the addendum; therefore, whether the union proceeds by $\alpha\beta$ or $\alpha\delta$ addition the *tert.* bromide should result. Polymol. (3) is the single intermol. structure that can lead to abnormal addition and only when the difference between the affinity relations of the unsaturated carbons of the compound for the components of HBr is overcome by the added negative influence of the oxygens. If the latter influence is greater, then the α - may become relatively negative to the β -C and, in thus reversing the affinity relations, O₂ and peroxides may cause a corresponding reversal in the mode of addition. If the negative influence of the O₂ or peroxide is insufficient to alter noticeably the positive-negative relationship of the unsaturated C, no reversal effect is apparent as exemplified in the alkene and unsaturated acid series. However, by increasing the oxidant influence of the catalyst, e.g., using hypohalous acid, abnormal additions can be brought about that cannot be effected either by O₂ or by a peroxide.

H. W.

Solvent and peroxide effect in the addition of hydrogen bromide to trimethylethylene. A. MICHAEL and N. WEINER (J. Org. Chem., 1939, 4, 531—541).—Ascaridole (I) causes the formation of "abnormal" CHMePr^oBr from CMe₂:CHMe (II) and HBr, the extent of the effect increasing with the concn. of (I). Contrary to Kharasch, therefore (cf. A., 1939, II, 530), abnormal addition is not limited to Δ^o -alkenes. In CS₂, pentane, and EtOAc at -78°, HBr and (II) give the (normal) CMe₂EtBr whereas in Et₂O at -78° they yield the abnormal bromide in considerable proportion which increases with rise in temp. It is reduced only slightly by the presence of "antioxidant" NHPH₂ but to a large extent by quinol (III). Under the above conditions, (II) and HCl or HI yield only the *tert.*-amyl halides. AcOH induces the formation of a small proportion of the abnormal *sec.* bromide; the amount, not affected by the presence of (I), is reduced slightly by NHPH₂ and completely by (III). In COMe₂ the addition yields only the *tert.* bromide, as it does also in the presence of (I). At -78° MeOH and EtOH effect a small % of the abnormal addition, which decreases with rise of temp. In these solvents (I) causes a large proportion of the abnormal addition at -78° but its effect falls off with rise in temp. and at 20° it has no measurable influence on the normal course of the reaction. The chemical mechanism for the peroxide effect, advanced by Kharasch, is not applicable to explain the above results of certain solvents in causing the abnormal addition or to interpret the sp. combined effect of solvent and peroxide. In the abnormal addition to (II) the relations between solvent effect and peroxide effect vary decidedly when used separately and together. The abnormal effect of solvents on the addition of HBr to (II) is sp., depending on their chemical character. In certain solvents (I) exercises a marked effect on the course of the addition whilst in other solvents it remains inert. The influence of NHPH₂ as "antioxidant" depends on the nature of the solvent and it may be practically ineffective in reducing the abnormal addition which is usually suppressed by (III); in some solvents, however, this effect is only partial and dependent on the temp. The relationships differ to a considerable extent from those observed in the corresponding reactions with Δ^o -alkenes. An explanation of the abnormal addition of HBr to (II) by solvent influence is advanced, based on the primary formation of double mols. of HBr and solvent. These then unite, in accordance with the partition principle, with the relatively more positive unsaturated C of the alkene and reversal occurs when the formed, unsaturated C-solvent-HBr grouping functions as relatively negative to the

terminal, formerly relatively negative, unsaturated C. A corresponding chemical change is believed to take place in the addition reversal by peroxide effect.

H. W.

Influence of the nature of the substituent on the velocity of catalytic hydrogenation of certain tri-substituted ethylenes, in presence of platinum. B. A. KAZANSKI and G. T. TATEVOSJAN (J. Gen. Chem. Russ., 1939, 9, 145S—1464).—The velocity of hydrogenation of substituted ethylenes (at 18°/760 mm.) falls in the order $\text{C}(\text{Et})_2\text{:CHMe} > \text{CPhMe:CHMe} \gg \text{CPh}_2\text{:CHMe} > \text{CPh}_2\text{:CHPh}$. In binary mixtures hydrogenation of both components proceeds simultaneously, but at different velocities. R. T.

Condensation of olefines and paraffins by means of sulphuric acid. H. I. WATERMAN, J. J. LEENDERTSE, and R. HESSELINK (Rec. trav. chim., 1939, 58, 1040—1047; cf. Brich *et al.*, B., 1938, 1007).—*iso*Pentane, b.p. 28—29° (I part), and "trimethylethene" (mainly $\text{CHMe}_2\text{:CHMe}$), b.p. 35—36° (3 parts), added to 98% H_2SO_4 at 0—9°, after 22—40 min. give a good yield of saturated hydrocarbons of higher mol. wt. Use of the sp. refraction method of Vlughter *et al.* (B., 1935, 836) shows that cyclic compounds are almost completely absent. Thus the main reaction is condensation of paraffins and olefines, followed by decomp. into paraffins and olefines with different nos. of C atoms, which react further. H_2SO_4 has some destructive action, as some CHMe_3 is formed, but the catalyst can be used several times without decrease in activity. Reactants in proportions 1:1 give a less saturated product and a lower yield (*loc. cit.*). A. T. P.

Hydrogenation of substituted acetylenes with Raney nickel. K. N. CAMPBELL and M. J. O'CONNOR (J. Amer. Chem. Soc., 1939, 61, 2897—2900).—Hydrogenation of substituted acetylenes in abs. MeOH in presence of Raney Ni can always be interrupted so as to yield readily the derived ethylenes, but the rate of hydrogenation shows a break after absorption of 2 H which is more distinct in the order, $(\text{:CPh})_2 > (\text{:CAlk})_2 > \text{CAlk:CAlk}' > \text{CPh:CH}$, CPh:CHMe (no break). Continued hydrogenation yields pure saturated hydrocarbons, except in the case of C_2Ph_2 which gives only *isostilbene*. The following are incidentally prepared: *ethyl*-, b.p. 87°/99 mm., *n-propyl*-, b.p. 104.5°/97 mm., and *n-butyl*-, b.p. 113°/61 mm., *isomylacetylene*; Δ^3 -*octene*, b.p. 127°/746 mm.; Δ^7 -*nonene*, b.p. 147.4°/740 mm.; Δ^6 -*decene*, b.p. 169.6°/746 mm.; η -*methyl- Δ^7 -octene*, b.p. 140.7°/746 mm.; *o-methyl- Δ^8 -nonene*, b.p. 163.2°/746 mm.; Δ^6 -*undecene*, b.p. 191.2°/750 mm. R. S. C.

Halogenation of hydrocarbons. Chlorination of olefines containing an unsaturated *tert.* carbon atom. J. BURGIN, W. ENGS, H. P. A. GROLL, and G. HEARNE (Ind. Eng. Chem., 1939, 31, 1413—1419; cf. A., 1939, II, 529).— Cl_2 and $\text{CMe}_2\text{:CH}_2$ give, as primary products, $\text{CH}_2\text{:CHMe-CH}_2\text{Cl}$ (I), $\text{CMe}_2\text{:CHCl}$, and $\text{CMe}_2\text{Cl-CH}_2\text{Cl}$, side-reactions being $\text{CMe}_2\text{:CH}_2 + \text{HCl} \rightarrow \text{Bu}^t\text{Cl}$, (I) + $\text{Cl}_2 \rightarrow \text{CHCl:CMe-CH}_2\text{Cl}$ (II) and $\text{CH}_2\text{:C(CH}_2\text{Cl)}_2$ (III), and (I) + $\text{HCl} \rightarrow \text{CMe}_2\text{Cl-CH}_2\text{Cl}$. If the contact time is reduced by mixing Cl_2 and $\text{CMe}_2\text{:CH}_2$ (a 1:1.5 mol. mixture is most effective) in a jet and passing the

mixture into a large reaction vessel (apparatus described), the side-reactions are reduced and there are obtained (I) 87, $\text{CMe}_2\text{:CHCl}$ 3, Bu^tCl 1, $\text{CMe}_2\text{Cl-CH}_2\text{Cl}$ 6, (II) + (III) 2, and trichlorides 1 mol.-%. The ratio, (I) : $\text{CMe}_2\text{:CHCl}$, is unaffected by change of conditions. Illumination, but not rise in temp. (cf. Kondakov, J. Russ. Phys. Chem. Soc., 1885, 17, 290), presence of liquid, surface, pressure (up to 50 lb. per sq. in.), or presence of H_2O , O_2 , or N_2 increases the proportion of addition of Cl_2 . Reaction is slow in the vapour phase, even at 150° for pure reactants, but light, presence of liquid (impurities, reactant, or products), or catalytically active surface accelerates the vapour reaction. Chlorination is exothermic (probably ~26 kg.-cal. per mol.) and use of liquid $\text{CMe}_2\text{:CH}_2$ helps to control the plant-scale reaction by virtue of its latent heat of vaporisation. Addition of HCl to $\text{CMe}_2\text{:CH}_2$ or (I) vapour is slow even in presence of light. Contrary to Kondakov (*loc. cit.*), (I), but not $\text{CMe}_2\text{:CHCl}$, is readily hydrolysed to Pr^tCHO , the case of hydrolysis at 100° being (I), $\text{Bu}^t\text{Cl} \gg \text{CMe}_2\text{Cl-CH}_2\text{Cl}$, (II), (III) $\gg \text{CMe}_2\text{:CHCl}$. "*tert.*-Amylene" ($\text{CMe}_2\text{:CHMe} + \text{CMeEt:CH}_2$) and Cl_2 give more additive products, viz. $(\text{CH}_2\text{:CMe-CHMeCl} + \text{CHMe:CMe-CH}_2\text{Cl})$ (tautomers giving always a ~3:2 mixture) 80, CMe_2EtCl 3, $(\text{CMe}_2\text{:CMeCl} + \text{CMeEt:CHCl})$ 3, di- 10 and trichlorides 4%. These products are less stable than those from $\text{CMe}_2\text{:CH}_2$ and, on a small scale, rise in temp. must be avoided by using capillary reaction tubes. Physical consts. of the products are given. R. S. C.

Peroxide effect in the addition of reagents to unsaturated substances. XXII. Addition of hydrogen bromide to trimethylethylene, styrene, crotonic acid, and ethyl crotonate. C. WALLING, M. S. KHARASCH, and F. R. MAYO (J. Amer. Chem. Soc., 1939, 61, 2693—2696; cf. A., 1939, II, 530).—In absence of air and presence of quinol, or NHPh_2 , HBr adds to $\text{CMe}_2\text{:CHMe}$ alone or in C_5H_{12} to give mainly CMe_2EtBr . However, in C_5H_{12} in presence of lauroyl peroxide (I), 64% of CHMePr^tBr is formed. In PhNO_2 100% and in pure EtBr 60% of CMe_2EtBr is formed even in presence of (I). Smith's failure (A., 1938, II, 258) to obtain CHMePr^tBr may have been due to its ready isomerisation by acid. Similarly, CHPh:CH_2 gives CHPhMeBr alone or in C_5H_{12} in presence of NHPh_2 , gives 80% of $\text{CH}_2\text{Ph-CH}_2\text{Br}$ in presence of peroxides in C_5H_{12} , but only 7% of the latter product in presence of peroxides without a solvent. $\text{CHMe:CH-CO}_2\text{H}$ and $\text{CHMe:CH-CO}_2\text{Et}$ give β -Br-derivatives under all conditions tried. R. S. C.

Manufacture of carbon tetrachloride.—See B., 1939, 1209.

Interaction of δ -halogeno- Δ^8 -butadienes with Grignard reagents.—See B., 1939, 1210.

Allylic rearrangements. IX. Isolation and rearrangement of primary and *sec.* pentenyl, hexenyl, and heptenyl bromides. W. G. YOUNG, L. RICHARDS, and J. AZORLOSA (J. Amer. Chem. Soc., 1939, 61, 3070—3074; A., 1939, II, 132).—Interaction of the corresponding $\text{CHR:CH-CH}_2\text{-OH}$ with 48% HBr —95% H_2SO_4 and fractionation of the

product at 1—5 mm. gives 80—90% of Δ^{β} -*n*-butenyl, b.p. 49°/93 mm., -pentenyl, b.p. 43·5°/30 mm., -hexenyl, b.p. 28°/9 mm., and -heptenyl bromide, b.p. 32°/3 mm., with small amounts of γ -bromo- Δ^{α} -*n*-butene, b.p. 31°/93 mm., -pentene, b.p. 30·5°/30 mm., -hexene, b.p. 22°/9 mm., and -heptene (impure), b.p. 23—25°/3 mm. The bromides are equilibrated at higher temp. The ease of equilibration is $C_4 > C_6 > C_5 > C_7$. The % of primary bromide in the equilibrium mixture is C_4 85·5, C_5 80·1, C_6 85·8, and C_7 ~89. Purity and composition (of mixtures) are determined by *n*, the results agreeing with those of ozonolysis, but not of Raman spectroscopy.

R. S. C.

Utilisation of aliphatic nitro-compounds.
Preparation of amines and oximes. K. JOHNSON [with E. F. DEGERING] (J. Amer. Chem. Soc., 1939, 61, 3194—3195).—Fe-HCl or H_2 -Raney Ni in MeOH or EtOH at 45—50°/6—110 atm. reduces aliphatic NO_2 -compounds to the derived amines in excellent yield. Zn dust in AcOH gives the oximes, which by subsequent hydrolysis give 43% of the aldehyde; some reduction to amine also occurs. R. S. C.

Loss of optical activity in the reaction of optically active erythro- and threo- γ -bromobutan- β -ols with hydrobromic acid. S. WINSTEIN and H. J. LUCAS (J. Amer. Chem. Soc., 1939, 61, 2845—2848).—When boiled with $Ac_2O \cdot CCl_4$ in presence of brucine, *dl*-erythro- γ -bromobutan- β -ol gives (+)-erythro- γ -bromobutan- β -ol (I) and (–)-erythro- γ -bromo- β -acetoxybutane (II), and *dl*-threo- γ -bromobutan- β -ol gives (–)-threo- γ -bromobutan- β -ol (III) and (–)-threo- γ -bromo- β -acetoxybutane (IV). Some stereomutation occurs in both cases and resolution is incomplete. (I) gives a (+)-*trans*-oxide, and (III) gives a *meso-cis*-oxide. $(CHMeBr)_2$ prepared from (I), (II), (III), or (IV) is inactive, thus supporting the reaction mechanism previously (A., 1939, II, 401) proposed. Other mechanisms are discussed and rejected. R. S. C.

Manufacture of esters of $\Delta^{\alpha\gamma}$ -butadien- β -ol.—Sec B., 1939, 1211.

Polarisations and related data of optically active and racemic β -octanol. J. B. M. COPPOCK and F. R. GOSS (J.C.S., 1939, 1789—1792).—Determinations of *d*, ϵ , mol. and partial polarisation in C_6H_6 of *d*-, *l*-, and *dl*- β -octanol (I) reveal no difference between the active and the racemic forms. These results are in agreement with the view that *dl*- β -octanol is simply a racemic mixture. The hygroscopic nature of the carbinol leads to anomalous results for the moist material and the need for careful exclusion of H_2O in the measurements described is emphasised. The apparent dipole moment of (I) in C_6H_6 is 1·66, and various vals. of $[\alpha]_D^{20}$ at different λ for the *d*- and *l*- β -octanol are recorded. J. D. R.

Preparation of higher tertiary alcohols. V. V. KORSCHAK (J. Gen. Chem. Russ., 1939, 9, 1470—1472).—Cetyl bromide, Et stearate (I), and Mg in Et_2O afford dotriacontane and *dihexadecylheptadecylcarbinol*, m.p. 45—46°. PhBr and (I) similarly yield *diphenylheptadecylcarbinol*, m.p. 51—52°, readily eliminating H_2O when distilled in vac., with produc-

tion of $\alpha\alpha$ -diphenyl- β -heptadecylethylene, b.p. 228—230°/10 mm., m.p. –6° (dibromide, m.p. 34°). PhBr, stearone, and Mg in $(C_5H_{11})_2O$ yield *phenyldiheptadecylcarbinol*, m.p. 46—47°, which with HBr gives *phenyldiheptadecylmethyl bromide*, m.p. 70—71°.

R. T.

Oxidation of $\alpha\beta$ -glycols or $\alpha\beta\gamma$ -polyalcohols by lead tetra-acetate in aqueous solution. E. BAER, J. M. GROSHENTZ, and H. O. L. FISCHER (J. Amer. Chem. Soc., 1939, 61, 2607—2609).—Oxidations are effected in excellent yield by adding $Pb(OAc)_4$ in AcOH to the glycol in H_2O ; the products are the same as are obtained in anhyd. solvents, unless hydrolysis occurs after oxidation. $\alpha\beta\epsilon$ -Diisopropylidene-*d*-mannitol thus yields 98·8% of *d*-OH-CH₂-CH(OH)-CHO, hydrolysis occurring during pptn. of the Pb by $N-H_2SO_4$. By subsequent oxidation with Br *d*-(–)-glyceric acid is prepared in 76% yield. Pinacol gives 95% of $COMe_2$. Me quinate consumes 2 $Pb(OAc)_4$, giving HCO_2H and $(CHO \cdot CH_2)_2C(OH) \cdot CO_2Me$, which is oxidised by Br to citric acid, isolated in 86% yield. R. S. C.

Formation of complex ethers and of acraldehyde during distillation of glycerol.—Sec B., 1939, 1209.

Sulphonation reactions with sulphuryl chloride. M. S. KHARASCH and (MISS) A. T. REID (J. Amer. Chem. Soc., 1939, 61, 3089—3092).— C_5H_5N and quinoline derivatives in light catalyse sulphonation of aliphatic hydrocarbons by SO_2Cl_2 (best added gradually so as to reduce the excess temporarily present) and depress the chlorination (cf. A., 1939, II, 497). Compounds of mercaptan, sulphide, or selenide type are less effective, anthraquinonesulphonic acids still less so. SO_2 and peroxides are quite ineffective. No sulphonation occurs in the dark. $SO_2 + Cl_2$ is ineffective and rise in temp. decreases the efficiency of SO_2Cl_2 by causing its dissociation. Many experiments are recorded with cyclohexane, but the reaction is general. Nuclei of aromatic compounds are unaffected. PhMe does not react, but PhEt gives some acid and PhBu⁺ gives fair yields of $CPhMe_2 \cdot CH_2 \cdot SO_3H$. Since SO_2Cl_2 sulphonates the nucleus of C_6H_6 derivatives in presence of $AlCl_3$, the above reactions occur by a free radical mechanism, involving SO_2Cl (cf. *loc. cit.*). R. S. C.

Formation of bis- β -diethylaminoethyl sulphide. E. S. COOK and C. W. KREKE (J. Amer. Chem. Soc., 1939, 61, 2971—2972).— $Br \cdot [CH_2]_2 \cdot NEt_2 \cdot HBr$ (prep. from $OH \cdot [CH_2]_2 \cdot NEt_2$, 66% HBr, and a trace of Br at 135°) and aq. NaHS at 55° give *di- β -diethylaminoethyl sulphide dihydrobromide*, m.p. 237·3—237·8° (corr.) [corresponding dihydrochloride, m.p. 245·5—247·5° (corr.)]. R. S. C.

Acetylene polysulphones. X. Vinyl chloride polysulphone. C. S. MARVEL and L. H. DUNLAP. XI. Compound, $C_{10}H_{16}O_2S$, from Δ^{α} -pentinene polysulphone. Other acetylene polysulphones. XII. Synthesis of 3:4- and 2:5-di-*n*-propyl-tetrahydrothiophen 1:1-dioxides. C. S. MARVEL and W. W. WILLIAMS (J. Amer. Chem. Soc., 1939, 61, 2709—2710, 2710—2714, 2714—2716).—X. Vinyl chloride polysulphone and 20% NaOH at 100° give

MeCHO (cf. A., 1938, II, 305) and the Cl is removed, but the S remains in org. combination. The sulphone is thus $[-SO_2 \cdot CHCl \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot]_n$. Hydrolysis gives $CHO \cdot CH_2 \cdot CH(OH) \cdot SO_2Na$ and thence MeCHO and $CHO \cdot CH_2 \cdot SO_2Na$ (polymerises). Pyrolysis in dioxan or treatment with liquid NH_3 causes complex reactions involving loss of Cl and S.

XI. Pyrolysis of the polysulphone from Δ^a -pentinene in dioxan produces an equilibrium mixture, the sole cryst. product of which is the substance, $C_{10}H_{16}O_2S$ (A., 1936, 1487). This is an $\alpha\beta$ -unsaturated sulphone, since it adds $CHNa(CO_2Et)_2$ in C_6H_6 , giving a substance, $C_{17}H_{28}O_6S$, m.p. $104.5-105^\circ$, and is reduced by $Zn-AcOH$ to a H_2 -derivative, m.p. $49-50^\circ$. H_2 -PtO₂-Pt-black gives an isomeric H_2 -derivative, m.p. $56.5-57^\circ$, unaffected by $Zn-AcOH$. Attempts to add reagents to other acetylene polysulphones led to cleavage. C_2H_2 gives no polysulphone. X-Ray diffraction patterns of fibres from Δ^a -pentinene, -hexinene, -heptinene, -noninene, and -pentadecinene polysulphones are unusually well-defined.

XII. $CHPr^a(CO_2Et)_2$, $CHPr^aBr \cdot CO_2Et$, and Na in xylene give 59% of Et_3 octane- $\delta\delta\epsilon$ -tricarboxylate, b.p. $182-183^\circ/1$ mm., hydrolysed by hot 40% KOH to an acid, which at room temp. gives CO_2 and *cis*-, m.p. $115-117^\circ$, and impure *trans*-($CHPr^a \cdot CO_2H$)₂. The Et_2 ester, b.p. $86-87^\circ/<1$ mm., thereof is hydrogenated (Cu chromite; dioxan; $260^\circ/300$ atm.) to 3:4-di-n-propyltetrahydrofuran (54.2%), b.p. $40-42^\circ/<1$ mm., and a little $\delta\delta$ -di(hydroxymethyl)-n-octane, b.p. $103^\circ/<1$ mm. The mixed products are converted by $HBr-AcOH$ at 125° (later $128-154^\circ$) into $\delta\delta$ -di(bromoethyl)-n-octane, b.p. $94^\circ/\sim 1$ mm., which with $Na_2S-EtOH$ gives 3:4-di-n-propyltetrahydrothiophen, b.p. $65-66^\circ/1$ mm. (1:1-dioxide, m.p. $57-59.5^\circ$). ($iC \cdot MgBr$)₂ and Pr^aCHO in Et_2O give Δ^a -n-decinene- $\delta\eta$ -diol, b.p. $113-114^\circ/1$ mm., hydrogenated (Raney Ni; a little EtOH; $75^\circ/298$ atm.) to n-decane- $\delta\eta$ -diol, m.p. $79-80^\circ$, the dibromide (prep. by HBr at $45-60^\circ$), b.p. $106-109^\circ/1$ mm., from which affords 2:5-di-n-propyltetrahydrothiophen, b.p. $74-75^\circ/1$ mm. (1:1-dioxide, b.p. $123-125^\circ/1$ mm.). SO_2 has a refractive const. 8.7.

R. S. C.

Identification of propionic acid in presence of acetic and butyric acids. L. MUSCANT and F. J. KASZUBA (J. Amer. Chem. Soc., 1939, 61, 2974-2976).—Propionyl derivatives are identified in presence of Ac and butyryl derivatives by hydrolysing, neutralising, evaporating, distilling the residue with H_3PO_4 , and identifying $EtCO_2H$ in the distillate microscopically as Hg^I salt. Formates in moderate amount interfere.

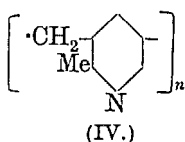
R. S. C.

Structure of vinyl polymerides. IV. Polymerides of methyl α -halogenoacrylates. C. S. MARVEL and J. C. COWAN. **V. Reactions of the polymerides of methyl vinyl ketone.** C. S. MARVEL and C. L. LEVESQUE (J. Amer. Chem. Soc., 1939, 61, 3156-3160, 3234; cf. A., 1939, II, 404).—IV. Me α -chloro- (I), b.p. $57-59^\circ/55$ mm., and α -bromo-acrylate (II), b.p. $72.5-74^\circ/78$ mm., prepared from $CH_2Hal \cdot CHHal \cdot CO_2Me$ by quinoline, polymerise when kept or, more rapidly, when warmed (35°) with Bz_2O_2 , to glassy or solid polymerides of

average mol. wt. $\sim 11,500$ (by η in dioxan), shown to be $[CH_2 \cdot CHal(CO_2Me) \cdot CHal(CO_2Me) \cdot CH_2]_x$ by reactions of the halogen. A sample of (I) which had polymerised very slowly was insol. and thus had a much higher mol. wt. Polymerised (I) or (II) liberates I from KI, the rate of reaction for polymerised (II) being comparable with that for $(CHBr \cdot CO_2Et)_2$ and \gg that for $CH_2(CHBr \cdot CO_2Et)_2$ or $Et_2 \gamma\epsilon$ -dibromo-n-heptane- $\gamma\epsilon$ -dicarboxylate (III). Zn eliminates 97% of HBr from both polymerides and heat causes loss of Br at a lower temp. than for (III) (this gives $EtBr$ when distilled in vac.). Quinoline removes ~ 1 HBr from polymerised (II). KI gives $[CH_2 \cdot C(CO_2Me) \cdot C(CO_2Me) \cdot CH_2]_n$, which, since it is insol., has many C:C replaced by cross-linkings although it reduces $KMnO_4$. Some cross-linking also occurs with Zn. Aq. $NaOH$ hydrolyses both polymerides to an acid,

$[CH_2 \cdot C(OH)(CO_2H) \cdot C(OH)(CO_2H) \cdot CH_2]_x$, which reduces HIO_4 in ~ 48 hr. (proof of $OH \cdot C \cdot C \cdot OH$) and HIO_3 . Treatment of $CH_2[CH(CO_2Et)]_2$ with $NaOEt-EtI$, hydrolysis by $KOH-(CH_2 \cdot OH)_2$, and decarboxylation by boiling, dil. HCl gives $CH_2(CH_2 \cdot CO_2H)_2$, the acid chloride of which with dry Br at 70° gives a product, converted by abs. $EtOH$ and subsequent distillation into the lactone, b.p. $134-138^\circ/3$ mm., of γ -bromo- ϵ -hydroxy- ϵ -carbethoxy-n-heptane- γ -carboxylic acid. HBr -abs. $EtOH$ then gives (III). Structures are supported by absorption spectra.

V. The head-to-tail structure (A., 1938, II, 126) of the polymeride of $COME \cdot CH \cdot CH_2$ is confirmed by con-

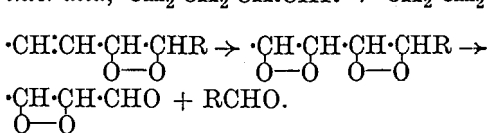


version of the polyketoxime by boiling $HCl-EtOH$ into the pyridine derivative (IV), containing $\sim 13.5\%$ of ketone (cf. Flory, A., 1939, II, 401). $NaOCl$ in aq. dioxan hydrolyses the

polymeride to the acid, $[CH_2 \cdot CH(CO_2H)]_x$.

R. S. C.

Antioxidants and the autoxidation of fats. [VIII.] Auto-oxidation of oleic acid, methyl oleate, oleyl alcohol, and *cis*- Δ^a -octadecene. F. E. DEATHERAGE and H. A. MATTILL (Ind. Eng. Chem., 1939, 31, 1425-1431; cf. B., 1937, 57).—When O_2 is passed through oleic acid, *cis*- Δ^a -octadecene, Me or Bu oleate, or oleyl alcohol (apparatus described) at 75° , the products include H_2O (25% of the O_2 consumed), peroxides (mostly volatile), peracids, small amounts of aldehydes (mostly further oxidised), acids, alcohols, esters, and epoxides [identified by hydrolysis by $AcOH$ at 100° to the $(OH)_2$ -compounds]. The rate of oxidation and consumption of O_2 ($2.83-1.55$ O_2 per C:C destroyed) decrease in the order of reactants named. Oxidation includes, *inter alia*, $CH_2 \cdot CH_2 \cdot CH \cdot CHR \rightarrow CH_2 \cdot CH_2 \cdot CH \cdot CHR \rightarrow$



R. S. C.

Synthetic glycerides of unsaturated fatty acids. I. Mono- and tri-linolein. H. C. BLACK and C. A. OVERLEY (J. Amer. Chem. Soc., 1939, 61, 3051-3052).—The relatively stable acid chloride

(prep. by SOCl_2), m.p. 59.5–60°, of the solid linoleic acid tetrabromide with $\alpha\beta$ -isopropylideneglycerol (1.03) or glycerol (0.32) and quinoline (1.03 mol.) in CHCl_3 gives *mono*-, m.p. 101.5–102°, and *tri-0- μ -tetrabromostearin*, m.p. 81–81.5°, debrominated by Zn in dry EtOH (not other conditions) to *mono*-, m.p. 14–15°, and *tri-linolein*, m.p. –5° to –4°, respectively. Rebromination gives 1:1 mixtures of *cryst.* and oily tetrabromoglycerides. R. S. C.

Rotatory power of zinc lactate. W. D. MACLAY, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, **61**, 3234–3235).—A correction (cf. A., 1939, II, 408). W. R. A.

Acetylation of lactic esters by keten. H. V. CLABORN and L. T. SMITH (J. Amer. Chem. Soc., 1939, **61**, 2727–2728).—Alkyl lactates are smoothly acetylated by keten in presence of a drop of H_2SO_4 . Me, b.p. 68–73°/14 mm., Et, b.p. 73–76°/11 mm., Bu^a, b.p. 94–97°/8 mm., Bu^b, b.p. 90–92°/9 mm., 205°/763–765 mm., Pr^a, b.p. 77–79°/7 mm., 196°/763–765 mm., Pr^b, b.p. 74–78°/9 mm., 183°/763–765 mm., n-, b.p. 101–103°/8 mm., 227°/763–765 mm., and *iso-amyl*, b.p. 107–110°/12 mm., 222°/763–765 mm., CH_2Ph , b.p. 145–148°/7 mm., and β -acetoxyethyl α -acetoxypropionate, b.p. 141–145°/10 mm., 265°/763–765 mm., are described.

R. S. C.

***tert*-Butyl esters of aliphatic dibasic acids.** H. J. BACKER and J. D. H. HOMAN (Rec. trav. chim., 1939, **58**, 1048–1061).—The corresponding acid chloride in C_6H_6 or CHCl_3 , Bu^vOH, and (a) $\text{C}_5\text{H}_5\text{N}$ or (b) NPhMe₂, afford: Bu^v₂ oxalate (a) (I), m.p. 70.5–71° (crystallographic properties), malonate (b), m.p. –7°, b.p. 93°/10 mm. (cf. A., 1939, II, 5; m.p. –14°), succinate (b), m.p. 36°, b.p. 115°/14 mm., glutarate (a), m.p. –10° to –11°, b.p. 125.5°/13 mm., adipate (a), m.p. 32.5°, b.p. 134°/10 mm. (cryst. properties), pimelate (b), m.p. –15°, b.p. 148°/11 mm., 125°/3 mm., suberate (a), m.p. 29°, b.p. 160°/11 mm., 134°/3 mm., azelate (a), m.p. –18°, b.p. 174°/13 mm., 145°/3 mm., and sebacate (a), m.p. 18°, b.p. 185°/13 mm., 154°/3 mm., respectively. The "oscillation" in m.p. is specially marked. Partial hydrolysis of the respective Bu^v₂ ester by KOH–EtOH gives the corresponding *K* Bu^v malonate, succinate, glutarate, and adipate, respectively, purified through the Bu^v H ester. (I) and KOH–EtOH gives mainly KEtC₂O₄, but aq. KOH–Bu^vOH affords *K* Bu^v oxalate. A. T. P.

Isotopic exchange reactions between deuterium oxide and *cis*- and *trans*-glutaconic acids. E. M. EVANS, H. N. RYDON, and H. V. A. BRISCOE (J.C.S., 1939, 1673–1679).—The partition of D and H between *cis*- and *trans*-glutaconic acids and 10% and 92% D₂O in presence of 1.05 mol. of NaOH is studied by heating the acid with D₂O, and determining the D in the water of combustion of the Ag salt by a micro-flotation method. The results show that three H are concerned in the tautomerism, and an estimate is made of the mobility of the tautomeric system. A special mechanism involving H-bond formation is advanced to explain the observed greater velocity of isotopic exchange in the case of the *cis*-acid. J. D. R.

Constitution of arabic acid. II. Degraded arabic acid. F. SMITH (J.C.S., 1939, 1724–1738; cf. A., 1939, II, 298).—Repeated methylation of degraded arabic acid with Me_2SO_4 –NaOH in COMe₂ gives a methylated degraded arabic acid, equiv. 830, which with MeI–Ag₂O yields a Me ester, hydrolysed by MeOH–HCl to a mixture from which the following are isolated: 2:3:4-trimethyl- α -methylglucuronoside (I) (3 mols.), 2:4-dimethyl- β - (II), m.p. 165–166°, and - α -methylgalactopyranoside (III), m.p. 105°, $[\alpha]_D^{18} +142^\circ$ in H₂O (α and β together, 3 mols.), 2:3:4-trimethyl- (IV) (5 mols.) and 2:3:4:6-tetramethyl-methylgalactoside (V) (1 mol.). The repeating unit of degraded arabic acid consists of 9 residues of galactose and 3 residues of glucuronic acid, and the identification of the methylated derivatives shows that 1:6- and 1:3-glycosidic links are present in the acids, and that the sugar units, all of which have pyranose rings, are joined in a branched-chain type structure, probably having four terminal residues. The structure of (I) is proved as follows: on heating with MeOH–HCl, the Me ester of (I) is formed, which with MeOH–NH₃ gives 2:3:4-trimethylmethylglucuronoside amide, m.p. 183°, $[\alpha]_D^{20} +137.5^\circ$ in H₂O, identical with that formed by the same method from esterified methylated glucuronolactone. 2:3:4-Trimethyl- β -methylglucuronoside, esterified with CH_2N_2 in Et₂O and treated with MeOH–NH₃, yields an amide, m.p. 193°, $[\alpha]_D^{20} -47^\circ$ in H₂O. When heated with N–H₂SO₄, (I) yields 2:3:4-trimethylglucuronic acid, which when oxidised with Br–H₂O followed by esterification (HCl–MeOH) gives 2:3:4-trimethyl-saccharolactone Me ester, identical with that formed by oxidation of 2:3:4-trimethyl- β -1:6-anhydroglucose with HNO₃. Oxidation of the Me ester of (I) with HNO₃ (*d* 1.42) yields Me *l*-(+)-threodimethoxy-succinate and methyl-*i*-xylotrimethoxyglutarate (isolated as the amides). The structure of (IV) is proved by its hydrolysis by N–H₂SO₄ to 2:3:4-trimethylgalactose monohydrate (VI), which is oxidised by Br–H₂O to 2:3:4-trimethylgalactonic acid (amide, m.p. 165°, $[\alpha]_D^{18} +32^\circ$ in H₂O) and by HNO₃ (*d* 1.42) to $\beta\gamma\delta$ -trimethylmucic acid [*diamide*, m.p. 273° (decomp.); *monoamide* Me₁ ester, m.p. 156° $[\alpha]_D^{18} +34^\circ$ in H₂O; *bismethylamide monohydrate*, m.p. 205°, $[\alpha]_D^{18} +7.5^\circ$ in H₂O]. α -Methylgalactopyranoside in $\text{C}_5\text{H}_5\text{N}$ with CPh₃Cl yields 6-triphenylmethyl- α -methylgalactopyranoside (a glass), $[\alpha]_D^{18} +30^\circ$ in COMe₂, which when repeatedly methylated (Me_2SO_4 –NaOH–COMe₂) yields 6-triphenylmethyl-2:3:4-trimethyl- α -methylgalactoside (a glass), $[\alpha]_D^{18} +44^\circ$ in CHCl₃, hydrolysed (HCl in Et₂O and then N–H₂SO₄) to (VI). The structure of (V) is proved by its hydrolysis (N–H₂SO₄) into 2:3:4:6-tetramethylgalactopyranose. The structure of (II) is proved by methylation (MeI–Ag₂O) to 2:3:4:6-tetramethyl- β -methylgalactoside, and by its hydrolysis (N–H₂SO₄) to 2:4-dimethylgalactose monohydrate (VII), m.p. 103°, $[\alpha]_D^{18} +122^\circ \rightarrow +85.6^\circ$ (equilibrium val.) in H₂O. The structure of (III) is proved as follows; hydrolysis with N–H₂SO₄ yields (VII); with NH₂Ph, (VII) gives 2:4-galactoseanilide, m.p. 216°; with NPhPh–NH₂, 4-methylgalactosephenylosazone, m.p. 150°, is formed, which on long keeping is converted into 4-methylanhydrogalactosephenylosazone, m.p. 158° (decomp.). Oxidation of (VII) with Br in H₂O gives

2:4-dimethyl-8-galactonolactone, m.p. 113° [α]_D²⁵ +162.2° \rightarrow +52.6° (equilibrium val.) in H₂O (phenylhydrazide, m.p. 183°; amide, m.p. 167° [α]_D¹⁸ +59° in H₂O). Oxidation of (VII) with HNO₃ followed by esterification with MeOH-HCl gives the *Me ester of α -dimethylmuco- β -lactone* (VIII), m.p. 111°, [α]_D¹⁴ +122° in H₂O \rightarrow +83.5° in 14 days (mutarotation still incomplete), which with MeOH-NH₃ gives the *diamide*, m.p. 229° [α]_D +30°, and with NH₂Me-MeOH, the *bismethylamide*, m.p. 214°, [α]_D¹⁵ +27° in H₂O, of α -dimethylmucic acid. Methylation of (VIII) (MeI-Ag₂O) gives *Me $\alpha\beta\gamma\delta$ -tetramethylmucate* and the *Me ester lactone of $\alpha\beta\gamma$ -trimethylmucic acid*, m.p. 63–64°, [α]_D¹⁸ +85° in H₂O, which with NH₃-MeOH gives the *diamide*, m.p. 225° (decomp.), and with NH₂Me-MeOH the *bismethylamide*, m.p. 232° (decomp.), [α]_D¹⁷ +23° in H₂O, of $\alpha\gamma\delta$ -trimethylmucic acid. J. D. R.

Oxidation of aldehydes. I. Combustion zones of butaldehyde, isobutaldehyde, propaldehyde, acetaldehyde, glyoxal, and acraldehyde. D. M. NEWITT, L. M. BAXT, and V. V. KELKAR. **II. Products of their combustion.** D. M. NEWITT and L. M. BAXT (J.C.S., 1939, 1703–1710, 1711–1720).—I. The combustion zones of PrCHO, Pr²CHO, EtCHO, MeCHO, (CHO)₂, and CH₂:CH·CHO have been mapped out over a wide range of temp. and pressure. Comparison of the combustion diagrams indicates that the order of reactivity of the saturated aldehydes with respect to O depends on the composition of the reacting medium and on its temp. and pressure. Presence of a side-chain increases the resistance of the aldehyde to attack by O and presence of a double linking alters the character of the combustion in such a way as to suggest that the processes occurring at low temp. result in the slower building up of the crit. concn. of the particular species responsible for cool-flame inflammation. The existence of three pressure limits of normal ignition has been observed in the case of saturated aldehydes.

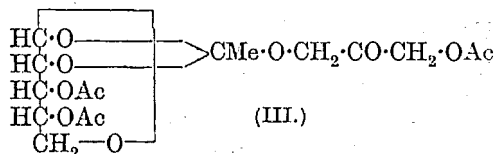
II. During oxidation of EtCHO and MeCHO the initial product is a relatively stable peroxide (I), which is found at all stages prior to cool-flame inflammation or normal ignition, and decomposes to a second peroxide and an alcohol; in aq. solution, (I) changes into a per-acid. The incidence of cool flames and normal ignition is shown to be conditioned by the presence of (I) in crit. concn. There is no evidence that per-acids or acids are formed in an excess aldehyde-O₂ medium during reaction, except at low temp. At low temp. some stepwise oxidation of aldehydes takes place, to give lower members of the series.

J. D. R.

Preparation of $\alpha\beta$ -unsaturated aldehydes.—See B., 1939, 1212.

Preparation of *d*- and *l*-ribosidodihydroxy-acetone tetra-acetates with an ortho-ester structure. C. W. KLINGENSMITH and W. L. EVANS (J. Amer. Chem. Soc., 1939, 61, 3012–3015).—*d*- (I), [α]_D²⁵ –56° in CHCl₃, or *l*-ribose tetra-acetate (II), m.p. 109.5–110°, [α]_D²⁵ +56° in CHCl₃, gives acetobromo-*d*-, [α]_D²⁵ –223.9° in CHCl₃, and *l*-ribose, m.p. 94.5–95.5°, [α]_D²⁵ +224.8° in CHCl₃, which with OAc·CH₂·CO·CH₂·OH and I in C₆H₆ give *diacetyl-d*-

(III), [α]_D²⁵ –11.6° in CHCl₃, and *l*-ribose-1:2-ortho-3'-acetoxylacetonyl acetate, m.p. 97–98°, [α]_D²⁵ +11.6° in CHCl₃, respectively, unstable to HCl and liberating >4 mols. of AcOH with alkali owing to liberation and decomp. of CO(CH₂·OH)₂. Equal amounts of (I) and



(II), when crystallised together, give *dl*-ribose tetraacetate, m.p. 90.5°, and yield (above reaction) the *dl*-form, m.p. 124.5–125°, of (III). M.p. are corr.

R. S. C.

Preparation of β -glucose. W. RASMUSSEN (Dansk Tidsskr. Farm., 1939, 13, 273–279).— α -Glucose is converted into β -glucose (I) by treatment (10% solution) with aq. Ca(HCO₃)₂ for 24 hr. at room temp. The solution is then brought to *p*_H 7.4 by heating to 40°, and after adding an equal vol. of COMe₂, is neutralised with H₂SO₄ and kept at 40° for 2 hr. The product on evaporation is entirely (I).

M. H. M. A.

Action of titanium tetrachloride on benzylglucopyranoside tetra-acetates. E. V. PIEL and C. B. PURVES (J. Amer. Chem. Soc., 1939, 61, 2978–2979).—Acetobromoglucose (prep. described), CH₂Ph·OH, and Ag₂O in Et₂O give β -benzylglucopyranoside tetra-acetate, [α] –53.2° in CHCl₃, which with TiCl₄ in boiling CHCl₃ gives an equilibrium mixture, whence α -benzylglucopyranoside tetra-acetate is isolated in 60% over-all yield. R. S. C.

Ketone sugar series. IX. Validity of Hudson's rules of isorotation in the *l*-sorbose series. β -Ethylsorbose and its tetra-acetate. E. PACSU (J. Amer. Chem. Soc., 1937, 59, 2669–2674; cf. A., 1937, II, 400).—Hudson's rules of isorotation hold for *l*-sorbose derivatives if the α_r consts. are applied separately to the α - and β -derivatives. A numerical factor, *F*, is introduced into the equations for [*M*] and it is suggested that *F* is contributed by varying ring-configurations of the two series. Only one *trans*- and one *cis*-form of hexopyranoses can exist, owing to steric hindrance by CH₂·OH and other groups. α -Sorbose tetra-acetate (I) and HCl in dry Et₂O give the syrupy acetochlorosorbose, which with abs. EtOH-Ag₂O affords a mixture, containing much ortho-ester; hydrolysis by hot, very dil. HCl converts the ortho-ester into (I), removal of which leaves β -ethylsorbose tetra-acetate, m.p. 86°, [α]_D²⁰ +82.7° in CHCl₃, hydrolysed by NaOMe-MeOH to β -ethylsorbose, a syrup, [α]_D²⁰ +31° in H₂O. The pyranoside structure of α -methyl- and β -ethyl-sorbose is proved by production of 1 mol. of HCO₂H by HIO₄.

R. S. C.

Ketone sugar series. X. Synthesis of a disaccharide, 1- β -glucosidofructose; structure of turanose and melezitose. E. PACSU, E. J. WILSON, jun., and L. GRAF (J. Amer. Chem. Soc., 1939, 61, 2675–2679).—Synthesis of the 1- β -isomeride and consideration of known reactions prove that turanose (I) is 3- α -glucosidofructopyranose. It follows that melezitose is the corresponding sucrose derivative.

Correct names for numerous derivatives described earlier are recorded. 2:3:4:5-Diisopropylidene- β -fructopyranose in CHCl_3 , when treated first with $\text{Ag}_2\text{O}-\text{CaSO}_4$ and then with I and acetobromoglucose at 55–60°, gives 1-tetra-acetyl- β -glucosido-2:3:4:5-diisopropylidene- β -fructopyranose, m.p. 162–163°, $[\alpha]_D^{20} -32.9^\circ$ in CHCl_3 , converted by hot $\text{NaOMe}-\text{MeOH}$ into 1- β -glucosido-2:3:4:5-diisopropylidene- β -fructopyranose, m.p. 174–175°, $[\alpha]_D^{20} -45.6^\circ$ in H_2O . 5% AcOH at 100° then yields 1- β -glucosidofructopyranose, +2 H_2O , m.p. 132–135°, $[\alpha]_D^{20} -59.2^\circ$ in H_2O , which reduces Fehling's solution but differs from (I) in being unaffected by yeast, not mutarotating in H_2O , and giving glucosazone only on rather long heating or in presence of an excess of AcOH . 3- α -Glucosido- β -methylfructopyranoside is obtained having m.p. 173–174°, $[\alpha]_D^{20} +3.6^\circ$ in CHCl_3 . R. S. C.

Relations between rotatory power and structure in the sugar group. XXXIV. Possibility of different conformations of the pyranoid ring. C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 2972; cf. A., 1939, II, 408).—The views of Pacsu (preceding abstracts) are borne out by earlier results of Hudson.

R. S. C.

Labiose, a new trisaccharide of the type of trehalose. S. M. STREPKOV (J. Gen. Chem. Russ., 1939, 9, 1489–1492).—The tubers of *Eremostachys labiosa* contain a non-reducing triose, termed labiose, +3 H_2O (I), m.p. 126–128°, $[\alpha]_D^{20} +136.7^\circ$ in H_2O (hexa-acetate, m.p. 88°, $[\alpha]_D^{20} +122.5^\circ$ in CHCl_3). (I) is hydrolysed by HCl or invertase, with production of 1 mol. of galactose and 2 mols. of fructose. Emulsion does not attack (I).

R. T.

p-Nitrophenyl- α -glucoside, m.p. 210°, $[\alpha]_D^{20} +215^\circ$ in H_2O .—See A., 1939, III, 1097.

Hexyl- and ethylhexyl-cellulose. Synthesis of (I) hexylcellulose, (II) ethylhexylcellulose. N. N. IZNAIRSKAJA (J. Appl. Chem. Russ., 1939, 12, 1050–1056, 1057–1059).—I. Mercerised cellulose, aq. NaOH , and $n\text{-C}_6\text{H}_{13}\text{Cl}$ heated at 125°/4 atm. for 16 hr. yield mono- and di-hexylcellulose. ($n\text{-C}_6\text{H}_{13}\text{O}$) is a by-product.

II. Ethylhexylcellulose (I) is prepared similarly, by adding EtCl to the reaction mixture. Films produced from (I) combine strength with resistivity to the action of H_2O .

R. T.

Bromoacetylcholine chloride, m.p. 138°, and the choline bromide ester of betaine bromide, decomp. 300°.—See A., 1939, III, 1096.

Amino-derivatives of pentaerythritol. IV. Tri(aminomethyl)hydroxymethylmethane. M. BEYAERT and F. GOVAERT (Proc. K. Akad. Wetensch. Amsterdam, 1939, 42, 776–789; cf. A., 1939, II, 534).— $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Br})_3$ (I) (cf. *ibid.*, 474) when heated with EtOH saturated with NH_3 at 125° for 20 hr. under pressure affords a product which with KOH followed by fractional distillation gives $\alpha\gamma$ -oxido- $\beta\beta$ -di(aminomethyl)propane monohydrate (II), b.p. 121–122°/15 mm. [hydrochloride, m.p. 234°; picrate, m.p. 237° (decomp.); oxalate, m.p. 154° (decomp.)] (converted by hot conc. HBr into $\alpha\gamma$ -diamino- β -bromomethyl- β -hydroxymethylpropane), and an inseparable mixture, b.p. $\sim 200^\circ/0.001$ mm.

B** (A., II).

(I) remains unchanged when dissolved in liquid NH_3 and with boiling $\text{EtOH}-\text{KOH}/0.5$ hr. affords $\alpha\gamma$ -oxido- $\beta\beta$ -di(bromomethyl)propane (III), b.p. 119/18 mm., which with liquid NH_3 at room temp. or aq. $\text{EtOH}-\text{NH}_3$ at 0° gives the dihydrobromide (IV), m.p. 224°, of anhyd. (II). (IV) with the theoretical amount of aq. KOH or with Ag_2O gives (II). (IV) with aq. NH_3 at 200°/12 hr. under pressure gives tri(aminomethyl)hydroxymethylmethane, m.p. 121° [hydrobromide, m.p. 302° (decomp.); tetra-acetate, m.p. 58°; nitrate, m.p. 239° (decomp.); sulphate, m.p. 288°; oxalate, m.p. 172° (decomp.)] [also obtained similarly from (III) or (II)]. J. L. D.

Amino-derivatives of pentaerythritol. V. Aminomethyltri(hydroxymethyl)methane. F. GOVAERT and M. BEYAERT (Proc. K. Akad. Wetensch. Amsterdam, 1939, 42, 790–797; cf. preceding abstract).—Pentaerythritol monobromohydrin (I) (cf. A., 1939, II, 199) with the theoretical amount of boiling $\text{EtOH}-\text{KOH}$ gives $\alpha\gamma$ -oxido- $\beta\beta$ -di(hydroxymethyl)propane (II), m.p. 84° (diacetate, b.p. 146°/12 mm.), converted by H halides into the halogen analogues of (I) and by H_2O at 150°/20 hr. (sealed tube) into pentaerythritol. (II) with aq. NH_3 at 200°/24 hr. under pressure gives aminomethyltri(hydroxymethyl)methane, m.p. 207° (tetra-acetate, b.p. 173°/0.4 mm.; oxalate, m.p. 206°; picrate, m.p. 98°), isolated through the carbamate, decomp. at 149°.

J. L. D.

Carbamates of α -amino-acid esters and their polycondensation. M. FRANKEL, O. NEUFELD, and E. KATCHALSKI (Nature, 1939, 144, 832–833; cf. A., 1939, II, 535).—On passing CO_2 through well-cooled $\alpha\text{-NH}_2$ -acid esters, alone or in Et_2O , cryst. products, $\text{CO}_2\text{R}'\cdot\text{CHR}\cdot\text{NH}\cdot\text{CO}_2\text{H}$, are produced. The "carbamates" of the Et esters of glycine, phenylglycine, and alanine thus prepared show different degrees of stability at low temp. At room temp. they decompose rapidly, giving off CO_2 . The new compounds assist in the poly-condensation of NH_2 -acids, since the tendency to condense is enhanced by the introduction of the readily-cleavable $\text{CO}\cdot\text{O}$ -group. On keeping for several weeks, glycine Et ester "carbamate" yields a mixture which contains, *inter alia*, glycine peptide esters of much higher chain length. Alanine Et ester "carbamate" yields a product which gives the biuret reaction, and from which tetra-alanine Et ester has been isolated.

L. S. T.

Oxidation of $d(+)$ -proline by d -amino-acid oxidase. H. A. KREBS (Enzymologia, 1939, 7, 53–57).—The oxidase (d -amino-acid deaminase) oxidises $d(+)$ -proline to δ -amino- α -ketovaleric acid, isolated as 2:4-dinitrophenylhydrazone, m.p. 223° [hydrochloride, m.p. 233–242° (decomp.); sulphate]. The oxidation of $d(-)$ -ornithine to the same aminoketo-acid proceeds at one fortieth and that of dl -pyrroline-2-carboxylic acid (double linking at 3:4) at 0.05 of the rate. The oxidation of $l(-)$ -proline by kidney possibly follows the same route as does that of $d(+)$ -proline, the primary product being probably δ -amino- α -ketovaleric acid. Relationships between NH_2 -acids of the ornithine group and those connected with proline are indicated. The general equation for the action of the oxidase is $\text{R}\cdot\text{CH}_2(\text{NHR}')\cdot\text{CO}_2\text{H} +$

$0.5\text{O}_2 = \text{R}\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{NHR}'$. In the case of proline there is only one product containing R and R'.

W. McC.

New synthesis of cystine. J. L. WOOD and V. DU VIGNEAUD (J. Biol. Chem., 1939, 131, 267—271).—With a view to the introduction of isotopic atoms, cystine is synthesised from simple materials. $\text{CH}_2\text{Ph}\cdot\text{SH}$ and polyoxymethylene with anhyd. HCl and CaCl_2 (cf. Böhme, A., 1936, 1092) give $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$ sulphide, b.p. $102^\circ/2$ mm., which does not condense successfully with $\text{CHNa}(\text{CO}_2\text{Et})_2$, but with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ gives *Et*₂ phthalimido-S-benzylthiolmethylmalonate, m.p. $81\text{--}82^\circ$ (all m.p. corr.), converted in aq. EtOH containing dioxan by $5\text{N}\cdot\text{NaOH}$ at 70° , followed by heating with conc. HCl and neutralisation by aq. NH_3 , into S-benzyl-dl-cysteine, m.p. $215\text{--}216^\circ$ (Ac derivative, m.p. 158° , identical with that prepared from l-cystine as starting material). This with Na in liquid NH_3 followed by NH_4Cl , extraction with Et_2O , neutralisation, and atm. oxidation (FeCl_3) gives a mixture of meso- and dl-cystine, separable by methods previously described (A., 1933, 89, 1149). The introduction of isotopic atoms is discussed.

E. W. W.

Asterubin, $\text{C}_5\text{H}_{13}\text{O}_3\text{N}_3\text{S}$, from starfish.—See A., 1939, III, 1062.

Alkylation of α -sulphonylamides. A. POMERANTZ and R. CONNOR (J. Amer. Chem. Soc., 1939, 61, 3139—3145).— $\text{RSO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ is incompletely alkylated by NaOEt and an alkyl halide in EtOH, but in C_6H_6 or PhMe alkylation is complete (most rapid with R_2SO_4), occurring mainly in the CH_2 but also on the N. Only one alkyl can be introduced into the CH_2 . Thus are obtained $\text{Bu}^n\text{SO}_2\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NH}_2$, m.p. $124\text{--}125^\circ$, α -n-butane- α' -sulphonyl-n-hexoamide, m.p. $110.5\text{--}111^\circ$ (corr.), α -p-toluenesulphonyl-n-hexoamide, m.p. $165.5\text{--}166^\circ$, and β -phenylpropionamide, m.p. $203\text{--}204^\circ$ (corr.), α -n-butane- α' -sulphonyl-n-butyrethylamide (I), m.p. $64.5\text{--}65^\circ$ (corr.), and α -n-butane- α' -sulphonylacetethylamide (II), m.p. 72° . $\text{SBu}^n\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (III) and NaOEt in PhMe give a N-Na derivative [a side-reaction also occurs, as acidification regenerates only part of the (III)], which with Et_2SO_4 gives the N-Et derivative, converted by H_2O_2 into (II). $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ and Bu^nSNa in H_2O give $\text{SBu}^n\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, b.p. $125\text{--}130^\circ/5\text{--}6$ mm., oxidised by 30% H_2O_2 to n-butane- α' -sulphonylacetic acid, m.p. $67.5\text{--}68.5^\circ$ (corr.), the acid chloride of which yields (II). The structure of (I) is proved by hydrolysis etc.

R. S. C.

Redistribution reaction. I. Random intermolecular exchange of organic radicals. G. CALINGAERT and H. A. BEATTY. II. Analysis of metal alkyl mixtures. Confirmation of random distribution. G. CALINGAERT, H. A. BEATTY, and H. R. NEAL. III. Determination of a material balance. G. CALINGAERT and H. SOROOS (J. Amer. Chem. Soc., 1939, 61, 2784—2784, 2755—2758, 2758—2760).—I. Reactions in which compounds of similar type are equilibrated with fission and reformation of covalent linkings are termed "redistribution reactions." Equilibration of metal alkyls, in which both the metal and alkyl may be different, is effected by many catalysts, e.g., metal halides and

metal alkyl halides, usually in hexane or decahydronaphthalene at 80° . No decomp. occurs; equilibrium is attained from either end. The products are formed in proportions strictly determined by the laws of probability and no notable energy changes occur. Evidence in favour of such random distribution of products is provided by the systems $\text{PbEt}_4\text{--PbMe}_4$, $\text{PbMeEt}_3\text{--PbMe}_3\text{Et}$, $\text{SnEt}_4\text{--SnMe}_4$, and $\text{SnMe}_4\text{--PbEt}_4$.

II. Analysis of mixed metal alkyls is described. Details are given proving random distribution of the products from the systems $\text{PbMe}_4\text{--PbEt}_4$, $\text{SnMe}_4\text{--SnEt}_4$, $\text{C}_2\text{H}_4\text{Cl}_2\text{--C}_2\text{H}_4\text{Br}_2$, $\text{SiEt}_4\text{--SiPr}_4$, $\text{HgMe}_2\text{--HgEt}_2$, and $\text{MeOAc--Pr}^i\text{CO}_2\text{Et}$.

III. By exactly determining the Pb in the various products, it is shown that no decomp. occurs when PbMe_4 and PbEt_4 are equilibrated to mixed Pb alkyls by AlCl_3 . 1.5% of the Pb was recovered as PbAlk_3Cl and a trace as PbCl_2 .

R. S. C.

Reaction between dimagnesium acetylenyl dibromide and carbonyl compounds. J. S. SALKIND and S. M. LABUZOV (J. Gen. Chem. Russ., 1939, 9, 1525—1532).—The velocity of reaction of $(\text{CMgBr})_2$ with aldehydes (MeCHO , EtCHO , PrCHO , PhCHO) is $>$ with ketones (COMe_2 , COMeEt , COMePr , COEt_2 , COPhMe , COPh_2), and falls with increasing mol. wt. of the compounds. In no case did the reaction proceed to conclusion, owing to occlusion of the reagent by reaction products.

R. T.

Optical activity dependent on the planar arrangement of the valencies of the 4-co-ordinated palladous atom. A. G. LIDSTONE and W. H. MILLS (J.C.S., 1939, 1754—1759).—*iso*Butylenediamine (improved prep.) and K_2PdCl_4 in H_2O yield *isobutylenediaminodichloropalladium*, decomp. $\sim 300^\circ$, which with mesostilbenediamine (I) and KI in H_2O yields dl-*isobutylenediaminemesostilbenediaminopalladous iodide*, m.p. 242° (decomp.) [monohydrate (II)]; when treated with Ag_2CO_3 and d(—)diacetyltartaric anhydride, followed by fractional crystallisation from aq. EtOH, d(—) (III) and l-*isobutylenediaminemesostilbenediaminopalladous d(—)diacetyltartrate dihydrate* (IV), $[\text{M}]_{\text{D}}^{25} -111^\circ$ in H_2O , are formed. [M] varies somewhat with concn. From (IV) by successive treatment with KI and AgNO_3 the nitrate, $[\text{M}]_{\text{D}}^{25} -50.4^\circ$ in H_2O , is formed; it is racemised only slowly by H_2O at 57° . (III) has $[\text{M}]_{\text{D}}^{25} +110^\circ$ and is converted by KI- AgNO_3 into the nitrate, $[\text{M}]_{\text{D}}^{25} +50.5^\circ$. When treated with dil. HCl, (II) yields PdCl_2 and (I). *r*-Stilbenediamine with dil. AcOH gives dl-*stilbenediamine diacetate monohydrate*, m.p. $131\text{--}132^\circ$, which when resolved through the *H* d-tartrate gives l-stilbenediamine (V). Both (I) and (V) are configurationally stable to boiling with dil. HCl for 16 hr. By the method described above, *isobutylenediamino-l-stilbenediaminopalladous iodide* is prepared, and converted by AgNO_3 into the nitrate, $[\text{M}]_{\text{D}}^{25} -62.4^\circ$, $[\text{M}]_{\text{D}}^{25} -497^\circ$, which is decomposed by KI-HCl into (V). The stability of the optical activity of the nitrates shows that the 4-covalent Pd must have a planar configuration of its valencies, since a regular tetrahedral arrangement would give a symmetrical configuration for the complex cation.

J. D. R.

Synthesis of some monosubstituted homologues of cyclopentane having a normal side-

chain. A. F. PLATE (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 257—262; cf. A., 1937, II, 236).— $n\text{-C}_5\text{H}_{11}\cdot\text{MgBr}$ (I) and cyclopentanone give $n\text{-amylcyclopentan-1-ol}$, dehydrated by aq. $\text{H}_2\text{C}_2\text{O}_4$ to $n\text{-amyl-}\Delta^1\text{-cyclopentene}$ (II), b.p. 177—179°/743 mm. (cf. Rinkes, A., 1938, II, 142). $\text{cyclopentenyl chloride}$ (III) and (I) give $n\text{-amyl-}\Delta^2\text{-cyclopentene}$ (IV), b.p. 173.5—175.2°/747 mm. (method: von Braun *et al.*, A., 1937, II, 404). Hydrogenation (Pd-black-EtOH) of (II) or (IV) at room temp. gives $n\text{-amylcyclopentane}$, b.p. 178—179°/752 mm. $1\text{-}n\text{-Hexylcyclopentan-1-ol}$ (modified prep.; cf. Zelinski *et al.*, A., 1933, 1150), b.p. 85—86°/4 mm., is dehydrated by aq. $\text{H}_2\text{C}_2\text{O}_4$ to $n\text{-hexyl-}\Delta^1\text{-cyclopentene}$ (V), b.p. 202—204.5°/743 mm., and some dodecane. (III) and $n\text{-C}_6\text{H}_{13}\cdot\text{MgBr}$ give $n\text{-hexyl-}\Delta^2\text{-cyclopentene}$, b.p. 196.8—198.8°/761 mm., reduced (Pd-black) in the cold [as also is (V)] to $n\text{-hexylcyclopentane}$, b.p. 201.1—202.2°/742 mm. $n\text{-Heptylcyclopentan-1-ol}$, b.p. 91—92°/3 mm., is readily dehydrated (I₂) to $n\text{-heptyl-}\Delta^1\text{-cyclopentene}$, b.p. 218—220°/762 mm., which is hydrogenated (Pd-black) at room temp. to $n\text{-heptylcyclopentane}$, b.p. 222.1—224°/741 mm. Physical consts. are recorded.

A. T. P.

Contact conversion of the six-membered into the five-membered ring. N. D. ZELINSKI and J. A. ARBUSOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 794—798).—When passed several times over Al_2O_3 (containing SiO_2) or once over SiO_2 gel at 450°, cyclohexene (I) is largely converted into $\text{methylcyclopentene}$. The product is hydrogenated ($\text{H}_2\text{-Pt-C}$; 150°) and then dehydrogenated (Pt-C ; 300°), the C_5H_6 [derived from unchanged (I)] is removed by 5% oleum, and the residue identified as $\text{methylcyclopentane}$ (A) by its physical consts. Passage of (A) in H_2 over platinised SiO_2 gel at 250° gives mixed paraffins, C_6H_{14} . $1\text{-Methyl-}\Delta^3\text{-cyclohexene}$ (II) similarly gives $\text{dimethylcyclopentenenes}$, converted as above into $\text{dimethylcyclopentanenes}$, b.p. 92—95°/755 mm., and paraffins, C_7H_{16} , b.p. 86—93°/761 mm. cyclohexane (III) and cyclopentene (IV) are unaffected by Al_2O_3 or SiO_2 gel at 450°, and it is thus only the cyclohexene ring which is isomerised. When passed in CO_2 over Cr_2O_3 at 450°, (I) gives H_2 , C_6H_6 , and a little cyclohexane . PhMe and a little methylcyclohexane are similarly obtained from (II), but (IV) and, unless the Cr_2O_3 is previously heated in H_2 at 450°, (III) are unaffected thereby.

R. S. C.

Isomerisation of cyclohexane under high pressure of hydrogen. S. ANDO (J. Soc. Chem. Ind. Japan, 1939, 42, 322—324B).— cyclohexane and H_2 passed over Mo_2S_3 at 200 atm. yield, at 380° 35%, and at 410° 80%, of $\text{methylcyclopentane}$. CH_4 and unsaturated hydrocarbons are not formed.

J. D. R.

Separation of the isomeric 1:4:2-dibromodinitrobenzenes and their reactions with $p\text{-phenylenediamine}$. C. J. SUNDE, G. JOHNSON, and C. F. KADE (J. Org. Chem., 1939, 4, 548—554).— $p\text{-C}_6\text{H}_4\text{Br}_2$ is nitrated (method: Jackson and Callhane, A., 1903, i, 159) and the product is poured on to ice and crystallised from AcOH , thereby giving 1:4:2-3- $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$ (I), m.p. 159—160°. The filtrate from (I) is pptd. by H_2O and the ppt. is crystallised

from dioxan, whereby 1:4:2:5- $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$ (II), m.p. 126—127°, is isolated. The residues from (II) are crystallised from EtOH or CS_2 , giving 1:4:2:6- $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$ (III), m.p. 119—120°. KNO_2 in boiling aq. EtOH followed by 12*N*- HCl converts (III) into 1:4:2:6- $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2$, m.p. 74—75°. $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and (I) in boiling MeOH containing KI , K_2CO_3 , and Cu-bronze give 3:6-dibromo-2-nitroanisole, m.p. 82.5—83°, in 5% yield, also obtained in the absence of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$. (I) is transformed by an excess of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in presence of K_2CO_3 , KI , and Cu-bronze into 3:6-dibromo-2-nitro-4'-aminodiphenylamine, m.p. 146—147°. $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and (II) in boiling EtOH containing NaOAc afford 4-bromo-2:5-dinitro-4'-aminodiphenylamine (IV), m.p. 180—181° (*Ac* derivative, m.p. 227—228°). Treatment of (IV) with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, Cu-bronze , KI , and anhyd. K_2CO_3 in boiling EtOH and of the product with an excess of Ac_2O at 100° gives the Ac_4 derivative of the Bandrowski base, m.p. 293—294°. 4-Bromo-2:5-dinitro-4'-acetamidodiphenylamine with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives the compound, $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_5\text{Br}$, m.p. 245—246°. (III), $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, and NaOAc in boiling EtOH yield 4-bromo-2:6-dinitro-4'-aminodiphenylamine (V), m.p. 193—194°, the *Ac* derivative, m.p. 271—272°, of which does not react with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH . With (III) and $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in the mol. ratio 2:1 the product is $\text{NN'-di-4-bromo-2:6-dinitrophenyl-}p\text{-phenylenediamine}$ (VI), m.p. 276—277°, also obtained from (V) and (III). 1:4:2:6- $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)_2$ and excess of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH containing NaOAc yield (V), and (VI) is obtained by means of (V) or by use of a deficiency of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$.

H. W.

Peroxide effect in the addition of reagents to unsaturated compounds. XXIII. Reaction of styrene with hydrogen sulphites. M. S. KHARASCH, R. T. E. SCHENCK, and F. R. MAYO (J. Amer. Chem. Soc., 1939, 61, 3092—3098; cf. A., 1940, II, 2).—Styrene with NaHSO_3 , KHSO_3 , or NHRR'R''SO_3 gives mainly (50—80%) $\beta\text{-hydroxy-}\beta\text{-phenylethane-sulphonic acid}$ (I) (*Na* salt) with less $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ (II) (*Na* and *Ba*, $+\text{H}_2\text{O}$, salts) and $\text{CHPh}\cdot\text{CH}\cdot\text{SO}_3\text{H}$ (III) (cf. A., 1939, II, 1). PCl_5 , followed by NH_3 , converts (I) into $\text{CHPh}\cdot\text{CH}\cdot\text{SO}_2\cdot\text{NH}_2$; (I) is isolated by fractionating the *K* or *Na* salts. The amounts of products formed from ammonium sulphites are independent of *R* (except for NPhMe_2) and are mainly determined by p_{H} . High O_2 pressure increases speed of reaction and favours formation of (III) by ammonium salts, but is without effect on amount of (III) formed by NaHSO_3 or KHSO_3 or of (I) formed by any salts. $[\text{HSO}_3]'$ does not affect the yields. Replacing O_2 by NO_2' or $\text{HS}_2\text{O}_8'$ leads to more (I) and (II) and no (III), but NO_3' does not cause reaction. (I), (II), and (III) are not interconvertible by acid, alkali, or $\text{NaHSO}_3\text{-O}_2$ [converts (III) into $\beta\text{-phenylethane-}\alpha\alpha\text{-disulphonic acid}$ (*Na*₂ salt, $+\text{2H}_2\text{O}$)], and are thus primary products. Reaction occurs thus: $\text{HSO}_3' + \text{oxidant} \rightarrow \text{HSO}_3 + [\text{oxidant}]'$; $\text{HSO}_3 + \text{CHPh}\cdot\text{CH}_2 \rightarrow \text{CHPh}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ (IV), followed by (a) (IV) $+\text{HSO}_3 \rightarrow$ (II) $+\text{SO}_3'$, (b) (IV) $+\text{oxidant} \rightarrow [\text{oxidant}]' + [\text{CHPh}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}]^+ \rightarrow (+\text{OH}') \quad (\text{I})$, (c) (IV) $+\text{O}_2 \rightarrow$ (III) $+\text{HO}_2$, or (d) $\text{HSO}_3 + \text{oxidant}$

$\rightarrow \text{SO}_3 + [\text{oxidant}]^- + \text{H}^+$. Mixtures of (II) and (III) are analysed by titrating with KMnO_4 , to which (II) is indifferent. $\text{NH}_2\text{Ph}\cdot\text{NH}_2$, β -phenylethane- $\alpha\beta$ -disulphonate (prep. from $\text{CHPhBr}\cdot\text{CH}_2\text{Br}$), m.p. 187—188° (decomp.), and - $\alpha\alpha$ -disulphonate, m.p. 195—200° (decomp.; rapid heating), and β -hydroxy- β -phenylethane- α -sulphonate, m.p. 180—181° (decomp.), are described. $\text{COPh}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ is unaffected by HSO_3^-O_2 . R. S. C.

Allen. I. Preparation of α -phenyl- $\Delta^{\alpha\beta}$ -butadiene. F. ACREE, jun., and F. B. LA FORGE (J. Org. Chem., 1939, 4, 569—574).—Gradual addition of α -chlorocrotonaldehyde in Et_2O to a solution of MgPhBr in Et_2O cooled in ice and salt yields β -chloro- α -phenyl- Δ^{β} -buten- α -ol, b.p. 122—124°/0.5—1 mm., m.p. 50—51°, also obtained by dehalogenation of $\beta\beta\gamma$ -trichloro- α -phenylbutan- α -ol by Zn dust in boiling EtOH . This is converted by HCl in C_6H_6 or by SOCl_2 into dichloro- α -phenylbutene, b.p. 100°/7 mm. (probable mixture of isomerides), which is dehalogenated (Zn dust in EtOH) to α -phenyl- $\Delta^{\alpha\beta}$ -butadiene (I), b.p. 44—47°/0.5—1.0 mm., which rapidly becomes yellow and viscous when exposed to air. PhBu^{α} is obtained by the hydrogenation (PtO_2 in EtOH) of (I). Combination does not occur between (I) and maleic anhydride or α -naphthaquinone. $\beta\beta\gamma$ -Trichlorobutanol is converted by MgPhBr into $\beta\beta\gamma$ -trichloro- α -phenylbutan- α -ol, b.p. 140—145°/0.5 mm., m.p. 53°, which is transformed by PCl_5 into $\alpha\beta\beta\gamma$ -tetrachloro- α -phenylbutane, b.p. 122—125°/0.5—1 mm., m.p. 54—55°, dehalogenated by Zn dust in boiling EtOH to (I). (I) is oxidised by KMnO_4 to BzOH and AcOH . H. W.

Diarylmethane derivatives. VII. Properties of the diphenylmethyl radical. W. T. NAUTA and D. MULDER (Rec. trav. chim., 1939, 58, 1070—1080).— CHPh_2Cl and mol. Ag in C_6H_6 in a vac. give (no coloration) 100% of $(\text{CHPh}_2)_2$ (I). In O_2 or NO (pale yellow) at atm. pressure, only 2—8% of (I) is isolated; the CHPh_2 radicals are removed by O_2 and afford, through a peroxide [probably $(\text{CHPh}_2)_2\text{O}_2$], $(\text{CHPh}_2)_2\text{O}$, m.p. 107—108°, COPh_2 , $\text{CHPh}_2\cdot\text{OH}$, and (?) CH_2Ph_2 . Mechanisms are discussed. Frequent production of (I) in many reactions (with CHPh_2X) is attributed to the formation of CHPh_2^{\cdot} . A. T. P.

Preparation of di-*o*-tolylmethyl chloride. E. B. REID (J. Amer. Chem. Soc., 1939, 61, 3238).— $(o\text{-C}_6\text{H}_4\text{Me})_2\text{CH}\cdot\text{OH}$ (prep. from the ketone by 2% Na-Hg), m.p. 120.5—121.5° (lit. 119—119.5°), and aq. $\text{HCl-C}_6\text{H}_6$ give 90% of di-*o*-tolylmethyl chloride, m.p. 70—71°. R. S. C.

Contact transformations of benzdicyclononene. N. V. ELAGINA and N. D. ZELINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 799—800).—Hydrogenation (Pd-C , first at 250° and then at 220°) of benzdicyclononene (Cook *et al.*, A., 1936, 321) gives much dicyclohexylmethane, converted by Pt-C at 300° into fluorene. R. S. C.

Diene syntheses. S. GONTSCHAROV (Inst. Chem. Tech. Ukrain. Acad. Sci., 1937, 3—83).—A review of known diene syntheses is given, and the possibilities of further applications of the reaction are discussed. R. T.

Synthesis of 9:10-dialkylanthracenes. W. E. BACHMANN and J. M. CHERMERDA (J. Org. Chem., 1939, 4, 583—587).—Anthrone is converted by Na and abs. EtOH followed by MeI into methylanthrone, which when dissolved in PhMe and added to MgMeI in Et_2O at 0° yields 9:10-dimethylanthracene (I), m.p. 180.5—181°, in 15—20% yield. 9:10-Dibenzylanthracene, m.p. 243—245°, is obtained similarly. Addition of anthraquinone (II) in Et_2O to MgMeI in the same solvent affords 9:10-dihydroxy-9:10-dimethyl-9:10-dihydroanthracene (III), m.p. 185—195° [since (II) dissolves sparingly in Et_2O it is necessary, in order to avoid undue bulk of solution, to place (I) in an extraction thimble so placed that the extract falls into the $\text{MgMeI-Et}_2\text{O}$]. (III) is transformed by $\text{C}_6\text{H}_6\text{-MeOH}$ containing a few drops of H_2SO_4 into 9:10-dimethoxy-9:10-dimethyl-9:10-dihydroanthracene, which with 2 equivs. of Na gives NaOMe and (I). Similarly, (II) and MgEtI afford 9:10-dihydroxy-9:10-diethyl-9:10-dihydroanthracene, m.p. 169—171° after softening, transformed into the 9:10- Me_2 ether, m.p. 179—180.5°, and thence into 9:10-diethylanthracene, m.p. 146—147°, in 95% yield; the picrate, m.p. 128—129°, is somewhat unstable and cannot be recrystallised without decomposition. 2-Methylanthraquinone and MgMeI give 9:10-dihydroxy-2:9:10-trimethyl-9:10-dihydroanthracene, m.p. 112—130°, which retains solvent of crystallisation very tenaciously and is analysed as the Me_2 ether, m.p. 181.5—182.5°; this is converted by Na in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ into 2:9:10-trimethylanthracene, two forms, m.p. 95—96° and 100—101°, respectively (picrate, m.p. 162—162.5°). If >2 equivs. of Na are used in the reaction the hydrocarbon which is formed reacts with the Na to give a deeply coloured 9:10- Na_2 compound. With exactly 2 equivs. of Na only the diol Me_2 ether enters into the reaction. H. W.

Synthesis of 2-methylphenanthrene from l-menthone. R. M. ORCUTT and M. T. BOGERT (J. Org. Chem., 1939, 4, 543—547).—When methyl-1-phenylethylcyclohexan-1-ols are cyclodehydrated, Me attached to $\text{C}_{(3)}$ of the cyclohexane nucleus cause the cyclisation to occur on $\text{C}_{(5)}$ of the same nucleus even when a Pr^{β} group is attached to this atom. Gradual addition of l-menthone in Et_2O to a solution of $\text{Ph}[\text{CH}_2]_2\text{MgBr}$ affords 1-phenylethyl-3-methyl-6-isopropylcyclohexanol, b.p. 167—169°/2 mm., which is dehydrated by PhNCO at room temp. to 1-phenylethyl-5-methyl-2-isopropyl- Δ^1 -cyclohexene, b.p. 145°/4 mm., highly unsaturated to Br in CCl_4 or KMnO_4 in COMe_2 and not cyclised by cold 90% H_2SO_4 . Conc. H_2SO_4 converts it into 2-methyl-12-isopropyl-1:2:3:4:9:10:11:12-octahydrophenanthrene (I), b.p. 123—127°/2 mm., which is indifferent towards Br in cold CCl_4 or KMnO_4 in COMe_2 . It is dehydrogenated by Se at 345—365° to 2-methylphenanthrene, m.p. 56° [picrate, m.p. 117.5—118.5° (corr.)]. (I) is oxidised by CrO_3 in boiling AcOH to 2-methyl-12-isopropyl-1:2:3:4:11:12-hexahydrophenanthraquinone (II), m.p. 151° (corr.) [quinoxaline derivative, $\text{C}_{24}\text{H}_{26}\text{N}_2$, m.p. 121° (corr.)], the colour of which is immediately discharged by $\text{Na}_2\text{S}_2\text{O}_4$. (II) is converted by cold aq. NaOH into 9-hydroxy-2-methyl-11-isopropyl-1:2:3:4:10:11-hexahydrofluorene-9-carb-

oxylic acid, m.p. 210—212° (corr.; decomp.), and is oxidised in boiling AcOH to 4-methyl-1-isopropyl-1:2:3:4:5:6-hexahydrodiphenyl-2:2'-dicarboxylic acid, m.p. 194—198° (corr.), with formation of a yellow anhydride. H. W.

Phenanthrene derivatives. IV. 9:10-cyclopenteno- and -hexeno-phenanthrene. C. K. BRADSHAW (J. Amer. Chem. Soc., 1939, 61, 3131—3132; cf. A., 1939, II, 499).— $\text{o-C}_6\text{H}_4\text{Ph-MgI}$ and cyclopentanone give a carbinol, dehydrated by KHSO_4 at 160° to 2- Δ^1 -cyclopentenylidiphenyl, b.p. 150—159°/5 mm. With $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in Et_2O this gives a crude epoxide, cyclised by 34% HBr-AcOH (1:1) to 9:10-cyclopentenophenanthrene, m.p. 150—151° [picrate, m.p. 164—165° (lit. 161.5—162°)], possibly by way of 2-2'-diphenylcyclopentanone. 2- Δ^1 -cyclohexenylidiphenyl, b.p. 183—193°/23 mm. (similarly prepared in 29% yield by using cyclohexanone), gives similarly 30% of 9:10-cyclohexenophenanthrene, m.p. 122—123° (lit. 120—121°).

R. S. C.

Thiocyano-derivatives of aniline and o-toluidine.—See B., 1939, 1213.

Reductive alkylation of aromatic primary amines. II. W. S. EMERSON and W. D. ROBB (J. Amer. Chem. Soc., 1939, 61, 3145—3146; cf. A., 1938, II, 439).—Hydrogenating NH_2Ar and RCHO in EtOH in presence of Raney Ni and NaOAc gives $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ (88%), $\beta\text{-C}_{10}\text{H}_7\cdot\text{NHR}$ ($\text{R} = \text{Et}$, Bu^a , or CH_2Ph , 50—64%), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHR}$ ($\text{R} = \text{Et}$ or Bu^a , 50—64%), $N\text{-}n\text{-butyl-}$ (80%), b.p. 155—167°/8 mm. (hydrochloride, m.p. 151—152°), and $N\text{-benzyl-}\alpha\text{-naphthylamine}$ (24%) (Bz derivative, m.p. 103—104°), $N\text{-ethyl-}$ (51%), b.p. 135—140°/20 mm. ($p\text{-C}_6\text{H}_4\text{Br}\cdot\text{SO}_2$ derivative, m.p. 113—114°), and $N\text{-}n\text{-butyl-}p\text{-anisidine}$ (65%), b.p. 142—145°/6 mm. (hydrochloride, m.p. 187.5—188°). 19% of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NBu}^a_2$ and 25% of $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NBu}^a_2$ are also obtained.

R. S. C.

New colour reaction for diarylamines. E. M. MEADE (J.C.S., 1939, 1808).— NHAr_2 and MgMeI in PhOMe, with BzCl, give a red colour. 1% of NHPh_2 in NPh_2Me is easily detected. 4'-Methoxy-4-methyl- or 4:4'-dimethoxy-diphenylamine, phenyl- α - and o- or $p\text{-anisyl-}\beta\text{-naphthylamine}$ give the test, but $N\text{-substituted NHPH}_2$, NH_2Ph , NHPHMe , NPhMe_2 , $\text{NHPH}\cdot\text{CH}_2\text{Ph}$, or $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ do not.

A. T. P.

Manufacture of pure sulphanilamide.—See B., 1939, 1293.

Organic salts of sulphanilamide and sulphanilysulphanildimethylamide. A. MOSSINI (Boll. Chim. farm., 1939, 78, 429—431).—Sulphanilamide in EtOH gives a *camphorsulphonate*, m.p. 175°. Sulphanilysulphanildimethylamide (I) similarly gives a *camphorsulphonate*, m.p. 195°. With phenylquinolinecarboxylic acid in EtOH, (I) gives products, m.p. 188° and 205°.

F. O. H.

Action of nitrous acid on dimethylaniline-*p*-sulphonic acid in sulphuric acid. (Miss) A. M. M. DAVIDSON and T. H. READE (J.C.S., 1939, 1701—1703).— $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (1 mol.) and HNO_2 (4 mols.) in H_2SO_4 (0.5—5N.) at 14° give mainly 3-nitro-

4-dimethylaminobenzenesulphonic acid (I) (anilide, m.p. 182°), and some $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (II) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO}$ (III) (with liberation of CH_2O) (cf. Michler *et al.*, A., 1882, 175). Yields of (I) and (III) increase, and of (II) decrease, with increase in concn. of H_2SO_4 ; (II) is converted into (III). 3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_3\text{H}$ refluxed with $\text{Cu-aq. NHMe}_2\text{-EtOH}$ gives (I). Solubility of (I) in H_2SO_4 (0.5 to 5N.) at 14° is recorded. A. T. P.

Diamidine derivatives.—See B., 1939, 1293.

Manufacture of solid diazonium salts.—See B., 1939, 1213.

Decomposition reactions of aromatic diazo-compounds. VII. Reactions of diazonium chlorides with esters and nitriles. W. E. HANBY and W. A. WATERS (J.C.S., 1939, 1792—1795; cf. A., 1938, II, 342).—Decomp. of solid ArN_2Cl under esters and nitriles with or without metals affords $\text{ArH} + \text{ArCl}$, but mainly tar. Decrease in activity is noted with ascending homologous series of esters.

$p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ (I), CaCO_3 , and MeOAc , EtOAc , or PrOAc give PhCl and $p\text{-C}_6\text{H}_4\text{Cl}_2$, but $\text{C}_5\text{H}_{11}\cdot\text{OAc}$ gives no simple product. Decomp. of PhN_2Cl in $\text{C}_5\text{H}_{11}\cdot\text{OAc}$, EtCO_2Pr , or MeOBz does not begin below 100° and is then uncontrollable; in MeOAc with Zn or Sb, ZnCl_2 or $\text{SbCl}_3 + (p\text{-C}_6\text{H}_4\text{Cl})_3\text{SbCl}_2$, respectively, are formed. $\text{C}_5\text{H}_{11}\cdot\text{OAc-Sb}$ do not react, and EtOAc-Te react slowly. (I) or PhN_2Cl and MeOAc , EtOAc , PrOAc , MeOBz , or HCO_2Pr give MeCHO (also formed in reactions with MeCN), but when the ArN_2Cl is freed from Et_2O (used for pptn. and washing), no aldehyde is obtained from MeOAc , and traces only from HCO_2Pr and EtCO_2Pr ; EtOAc gives MeCHO . (I)- PrOAc afford a little EtCHO . PhN_2Cl and Bu_2O , $(\text{C}_5\text{H}_{11})_2\text{O}$, or $\text{MeOAc-Bu}_2\text{O}$ give no RCHO . Formation of MeCHO by dehydrogenation of Et_2O by a free radical is discussed (cf. Evans *et al.*, A., 1939, II, 251). Decomp. of ArN_2Cl in $\text{RCN} + \text{CaCO}_3$ at 40° gives small amounts of ArH , ArCl , NHAcAr , and COArMe ; the two last reactions are distinctive of RCN , and suggest addition to CN of free radicals. PhN_2Cl , o- and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$, (I), and 4:1:2- and 5:1:2- $\text{C}_6\text{H}_3\text{ClMe}\cdot\text{N}_2\text{Cl}$ are investigated. EtCN is less reactive than MeCN ; PhN_2Cl thus affords only $\text{C}_6\text{H}_6 + \text{PhCl}$, and $\text{CH}_2\text{Ph}\cdot\text{CN}$ gives no simple product. All the reactions support the view that some decomp. of ArN_2Cl to neutral radicals can occur.

A. T. P.

Decomposition reactions of aromatic diazo-compounds. VIII. The diazocyanides. O. STEPHENSON and W. A. WATERS (J.C.S., 1939, 1796—1804).—The thermally stable *anti*-diazocyanides (A), $\text{ArN}\cdot\text{N}\cdot\text{CN}$, are converted photochemically in EtOH or COMe_2 into the isomeric, reactive, *syn*-diazocyanides (B) (cf. Hartley, A., 1938, II, 272). Pptn. of AgCN occurs when (A) in EtOH-AgNO_3 are exposed to light (not in the dark); eventually all the (A) decomposes to a colourless solution of a diazonium salt. With pure (A) alone, the photochemical change reaches an equilibrium val., overwhelmingly in favour of (A) (only a faint turbidity with AgNO_3). Solutions of (A) in EtOH or COMe_2 in closed vessels exposed to light for several days darken and give the same

products as those from thermal decomp. of the corresponding (*B*). There is little action in the dark. Cu has no direct effect on (*A*) in COMe₂ (N₂ is evolved in daylight; decomp. of *p*-chlorobenzene-*anti*-diazocyanide is examined). Under non-ionising solvents, there is no evolution of N₂ and (*A*) can be recovered unchanged even after exposure to light. In non-ionising solvents (CCl₄ convenient) quant. isomerisation of (*B*) to (*A*) occurs even in absence of light (cf. Le Fèvre *et al.*, A., 1938, II, 229). The dry solids do not isomerise in the dark. The differing behaviour of (*B*) in ionising and non-ionising solvents is due to the fact that (*B*) exist in EtOH in tautomeric equilibrium with the unstable diazonium cyanide (cf. Hantzsch, A., 1900, i, 567). Freshly prepared solutions of (*B*) in dil. EtOH with AgNO₃ give (rapidly) AgCN and a sol. colourless diazonium nitrate. Acidified (HNO₃) solutions of (*B*) are very stable and even after a time give quant. yields of AgCN and the filtrate couples instantly; a neutral solution of (*B*) in aq. EtOH decomposes quickly owing to hydrolysis and self-coupling, and does not give quant. pptn. of AgCN; the filtrate does not couple appreciably. The following are prepared: *p*-chloro- (I) and -bromobenzene-*syn*- (II); *o*-chlorobenzene-*syn*- (III), m.p. 49°, and -*anti*-, m.p. 78°; 4-chloro-*o*-toluene-*syn*- (IV), m.p. 49°, and -*anti*-, m.p. 68°; 5-chloro-*o*-toluene-*syn*- (V), m.p. 60°, and -*anti*-diazocyanide, m.p. 75°. Decomp. of (*B*) in CCl₄ is initiated by Cu (not by Ag, Hg, Fe, Pb, or Zn) and gives N₂, HCN, and 10–20% of ArCl: thus, (I) gives *p*-C₆H₄Cl₂; (III) gives *o*-C₆H₄Cl₂ + *o*-C₆H₄Cl-CN; (II) affords *p*-C₆H₄ClBr; (IV) gives 1:4:2-C₆H₃MeCl-CN (trace) and 1:2:4-C₆H₃MeCl₂; (V) affords 1:2:5-C₆H₃MeCl₂. In dry C₆H₆ + Cu, (*B*) gives HCN, N₂, and ArPh: (I) affords *p*-C₆H₄PhCl; (III) gives *o*-C₆H₄Cl-CN and *o*-C₆H₄PhCl; (II) gives *p*-C₆H₄Br-CN and *p*-C₆H₄PhBr; (IV) and (V) give traces of nitrile. Ag or Zn gives no reaction. Fe affords a trace of *p*-C₆H₄PhCl from (I). In EtOH alone, (*B*) give HCN + MeCHO and some ArH; in EtOH + Cu, small amounts of the respective ArCN are also formed. Hg, Sb, or Zn gives no reaction. In COMe₂ or MeOAc, (*B*) give HCN and some (*A*). In COMe₂ + Cu, no free HCN is formed; (III) gives PhCl + *o*-C₆H₄Cl-CN, and (IV) affords *p*-C₆H₄MeCl + 1:4:2-C₆H₃MeCl-CN. Hg, Sb, Zn, or Ag does not effect decomp. In dry Et₂O + Cu, (*B*) give MeCHO, HCN, and ArH: from (III), PhCl + *o*-C₆H₄Cl-CN; from (II), PhBr + *p*-C₆H₄Br-CN; from (IV), *p*-C₆H₄MeCl + 1:4:2-C₆H₃MeCl-CN; and from (V), *m*-C₆H₄MeCl + 1:5:2-C₆H₃MeCl-CN. (I) in cyclohexane gives *p*-C₆H₄Cl-CN. The Cu appears to be attacked only in CCl₄. Total % and N content of tar (not polyazo-compound) obtained as main product in decomp. of (*B*) is recorded, as also is % of diazo-group evolved as N₂. The theory of Hantzsch *et al.* (A., 1895, i, 348) is disputed. It appears that the radicals formed by decomp. of (*B*) react with vicinal solvent mols. and thus may have a free existence.

A. T. P.

Constitution of diazoamino-compounds. A. MANGINI (J.S.C.I., 1939, 58, 327–330).—The view of Dwyer (A., 1938, II, 483; cf. A., 1939, II, 543) that isomerism in nitrodiazoamino-compounds is due to

normal and *aci*- (quinonoid) forms is incompatible with the author's results (A., 1934, 68; 1935, 969; 1937, II, 454), in which isomerism is observed in *m*-NO₂-compounds. Any isomerism in this group is regarded as geometrical, but Dwyer's "*aci*-compounds" (*loc. cit.*) may be NH₄ salts. E. W. W.

Nitrosation of *m*-halogenophenols and their conversion into benzoquinonemonoximes. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1939, 1808; cf. A., 1930, 910).—*m*-C₆H₄Hal.OH (I) (Cl or Br) and aq. NaNO₂–50% aq. AcOH at <20° give good yields of 4:3:1-NO-C₆H₃Hal.OH. (I) (Cl, Br, or I) in AcOH with NaNO₂–conc. H₂SO₄ (previously heated to 70°) at <20°, then at 0°, give the respective *m*-halogeno-*p*-benzoquinoneoxime (cf. A., 1934, 181).

A. T. P.

Bromination of *p*-diphenyl acetate. S. E. HAZLER and H. A. KORNBERG (J. Amer. Chem. Soc., 1939, 61, 3037–3039).—Substitution of *p*-diphenyl benzoate and benzenesulphonate (A., 1937, II, 332; 1939, II, 369) is governed by steric hindrance, since the acetate, m.p. 87–88°, with Br (1 mol. at 100° or 2 mols. at 110°) gives 2-bromo-, m.p. 74–75° (also obtained from 4:2:1-C₆H₃PhBr.OH and Ac₂O–NaOAc at 100°), or 2:6-dibromo-4-diphenyl acetate, m.p. 81–83° (also obtained from 4:2:6:1-C₆H₂PhBr₂.OH by boiling Ac₂O–NaOAc). 4-Bromo-4-diphenyl acetate, m.p. 128–129°, is obtained by boiling the phenol with Ac₂O–NaOAc. R. S. C.

Synthesis of $\alpha\alpha\alpha$ -triphenyl- β -*o*-anisylethane. H. A. IDDLIS, K. S. FRENCH, and E. F. MELLON (J. Amer. Chem. Soc., 1939, 61, 3192–3194).—*o*-OMe-C₆H₄.CH₂.OH (prep. by electrolytic reduction of *o*-OMe-C₆H₄.CO₂H), b.p. 120–122°/12 mm., and conc. HCl–Et₂O give the chloride (I), b.p. 111–113°/14 mm., the Mg derivative of which with CPh₃Cl in boiling Et₂O–C₆H₆ gives $\alpha\alpha\alpha$ -triphenyl- β -*o*-anisylethane, m.p. 140–142°, obtained also from (I) by CPh₃Na in Et₂O and not identical with the methylation product, new m.p. 162–163°, derived from the rearranged *o*-cresol-CPh₃.OH compound (cf. Schorigin, A., 1927, 54; 1925, i, 1404; Boyd *et al.*, A., 1928, 516).

R. S. C.

Odour of alkoxydiphenyls. C. M. BREWSTER and I. J. PUTMAN, jun. (J. Amer. Chem. Soc., 1939, 61, 3083–3085).—The odour of *o*- or *p*-C₆H₄Ph.OH is not much affected by etherification, but the *o*- have stronger odours than have the *p*-ethers. Heating the appropriate phenol and alkyl halide with NaOH in COMe₂ give *o*-diphenyl *Pr*^a, b.p. 303°, Me, b.p. 288° (lit. 274°), Et, m.p. 34°, *Pr*^b, b.p. 315–317° (slight decomp.), allyl, b.p. 312° (darkens ~280°), and (slowly) CH₂Ph ether, b.p. 324° (slight decomp.), and *p*-diphenyl Et, m.p. 76°, Me, m.p. 90°, *Pr*^a, m.p. 76–77°, *Pr*^b, m.p. 73°, allyl, m.p. 86–87°, *Bu*^a, m.p. 74–75°, and CH₂Ph ether, m.p. 136°. R. S. C.

Rearrangement of phenyl allyl ethers. IV. Examination of the pyrolysis product of phenyl allyl ether for evidence of *p*-rearrangement. W. M. LAVER and R. M. LEEKLEY (J. Amer. Chem. Soc., 1939, 61, 3042–3043).—Pyrolysis of CH₂.CH.CH₂.OPh gives only *o*-allylphenol [also obtained by decarboxylating

3 : 4 : 1-CH₂:CH·CH₂·C₆H₃(OH)·CO₂H by a trace of Cu in boiling quinoline], since isomerisation by MeOH-KOH and subsequent ozonisation in EtOAc affords only *o*-OH·C₆H₄·CHO. 1% of *p*- can be detected in *o*-OH·C₆H₄·CHO by removing the latter from Et₂O as Cu salt. R. S. C.

Vitamin-E. XIX. Alkenylation of phenol with δ -chloro- and δ -bromo- Δ^{β} -hexene. Rearrangement of the phenyl ether. L. I. SMITH, H. E. UNGNADE, W. M. LAUER, and R. M. LEEKLEY (J. Amer. Chem. Soc., 1939, 61, 3079—3083).—CHMe:CH·CH₂·CH₂·X (X = Cl or Br; prep. from the alcohol by dry HCl-anhyd. Na₂SO₄ or 40% HBr, respectively), PhOH, and K₂CO₃ in COMe₂ give mixed ethers (with MgMeI show 0.9 active H by cleavage), mono- (A) and di-alkenylphenols (B), the amount of (B) being large if even 1 mol. of halide is used. (A) give mixed chromans and aryloxyacetic acids; small amounts of *o*-, m.p. 110—110.5°, and *p*- α -ethyl- Δ^{β} -butenylphenoxyacetic acid, m.p. 95.2—96°, are isolated. These acids with O₃ give MeCHO with a little CH₂O and are hydrogenated (PtO₂; dry Et₂O) to *o*- (I), m.p. 75—76°, and *p*- α -ethyl-*n*-butylphenoxyacetic acid (II), m.p. 82—83°, which are synthesised. The condensation thus gives a complex mixture containing small amounts of *o*- and *p*-OH·C₆H₄·CH₂·CH·CHMe. The Grignard reagent from *o*-C₆H₄Br·OMe (prep. from *o*-NO₂·C₆H₄·OMe by H₂-Raney Ni at 100°/80 atm. in EtOH, followed by a Sandmeyer reaction) and COEtPr^a (prep. from Pr^aCHO and MgEtBr and subsequent oxidation by Na₂Cr₂O₇-H₂SO₄) give a carbinol, converted by distillation at 1 atm. with 2 drops of H₂SO₄ into *o*-hexenylanisoles, which with H₂-PtO₂ in MeOH at 3 atm. give *o*- α -ethyl-*n*-butylanisole, b.p. 104—105°/9 mm., and thence (HI-AcOH-Ac₂O) *o*- α -ethyl-*n*-butylphenol, b.p. 109—111°/10 mm., and (I). *p*-OMe·C₆H₄·MgBr and COEtPr^a in Et₂O give similarly *p*-hexenyl- and *p*- α -ethyl-*n*-butylanisole, b.p. 125—125.5°/15 mm., *p*- α -ethyl-*n*-butylphenol, b.p. 134—145°/14 mm., and (II). (B) shows vitamin-E activity (50-mg. doses); other products were inactive. R. S. C.

Diarylmethane derivatives. VI. Occurrence of the di-*p*-anisylmethyl radical. W. T. NAUTA and D. MULDER (Rec. trav. chim., 1939, 58, 1062—1069; cf. A., 1939, II, 306).—CHCl(C₆H₄·OMe-*p*)₂ and mol. Ag in C₆H₆ and CO₂ give a transient red colour; the resulting colourless solution yields [CH(C₆H₄·OMe-*p*)₂]₂ (I) (100%), indicating that the radical CH(C₆H₄·OMe-*p*)₂ is completely dimerised. In presence of O₂, the initial red colour becomes orange-yellow to pale-brown; CO(C₆H₄·OMe-*p*)₂ (II) (main product), *p*-OMe·C₆H₄·CHO, and (?) *p*-OH·C₆H₄·OMe, are isolable. In an atm. of NO, some (II) and (I) are formed. (I) does not absorb O₂ in C₆H₆ at room temp., and there is no visible colour change when it is heated (alone or in xylene). A. T. P.

Synthesis of 1 : 4-dimethylphenanthrenes structurally related to morphol. J. T. CASSADAY and M. T. BOGERT (J. Amer. Chem. Soc., 1939, 61, 3055—3057; cf. A., 1939, II, 503).—2 : 3 : 4 : 1-NO₂·C₆H₂(OMe)₂·CHO and 2 : 5 : 1-C₆H₃Me₂·CH₂·CO₂K

(I) in Ac₂O at 105—110° give 2-nitro-3 : 4-dimethoxy- α -*p*-xylylcinnamic acid, m.p. 205.5—206.5°. 2 : 3 : 4 : 1-NO₂·C₆H₂(OMe)(OAc)·CHO and (I) in Ac₂O give 2-nitro-4-acetoxy-3-methoxy- α -*p*-xylylcinnamic acid, m.p. 211—214°. FeSO₄-aq. NH₃ then gives 2-amino-3 : 4-dimethoxy-, m.p. 110—113° (hydrochloride), and 2-amino-4-hydroxy-3-methoxy- α -*p*-xylylcinnamic acid, m.p. 203—204°, cyclised (Pschorr) to 5 : 6-dimethoxy-, m.p. 180.5—181.5°, and 6-hydroxy-5-methoxy-1 : 4-dimethylphenanthrene-10-carboxylic acid (acetate, m.p. 170.5—171.5°), distillation of which with Cu powder at 25 mm. yields 5 : 6-dimethoxy-, m.p. 73.5—74°, and 6-hydroxy-5-methoxy-1 : 4-dimethylphenanthrene, m.p. 136.5—137°, respectively. The OMe of the phenanthrene derivatives resists hydrolysis. M.p. are corr. R. S. C.

Alkaloids of plants of the Papaveraceæ family.

IV. Alkaloids of Roemeria refracta, D.C. Structure of roemerine and synthesis of 2 : 3-methylenedioxyphenanthrene. R. A. KONVALOVA, S. JUNUSOV, and A. P. ORÉKHOV (J. Gen. Chem. Russ., 1939, 9, 1507—1511; cf. A., 1939, II, 565).—6-Nitropiperonal, CH₂Ph·CO₂Na, and Ac₂O (100°; 24 hr.) yield 6-nitro-3 : 4-methylenedioxy- α -phenylcinnamic acid, m.p. 199—200°, reduced by FeSO₄ in aq. NH₃ (40 min. at 80°) to 6-amino-3 : 4-methylenedioxy- α -phenylcinnamic acid, m.p. 207—208°. Successive diazotisation and treatment with Cu powder at room temp. then gives 2 : 3-methylenedioxyphenanthrene-9-carboxylic acid, m.p. 255—256°, decarboxylated (Cu-Cr₂O₃ catalyst in quinoline; 1 hr. at the b.p.) to 2 : 3-methylenedioxyphenanthrene, m.p. 99—100° (picrate, m.p. 149—150°; Br₂-derivative, m.p. 228—229°). This is not identical with the product obtained from roemerine, the CH₂O₂ of which cannot therefore be in positions 2 : 3 or 6 : 7. R. T.

Application of the Pschorr reaction to *p*-xylylene-2 : 5-di-(6'-aminoveratrylideneacetic acid). Synthesis of 9 : 10-dimethyl-1 : 2 : 5 : 6-di-(3' : 4'-dimethoxybenz)anthracene. J. T. CASSADAY and M. T. BOGERT (J. Amer. Chem. Soc., 1939, 61, 3058—3061).—6 : 3 : 4 : 1-NO₂·C₆H₂(OMe)₂·CHO and 1 : 4 : 2 : 5-C₆H₂Me₂(CH₂·CO₂H)₂ in Ac₂O give *p*-xylylene-2 : 5-di-(6'-nitroveratrylideneacetic acid), decomp. >300°, reduced by FeSO₄-aq. NH₃ to the (NH₂)₂ acid (I), decomp. >300°, which, when diazotised (solution in aq. K₂CO₃-NaNO₂ run into 5*N*-H₂SO₄) and treated with Cu powder at 0—5°, gives *p*-xylylene-2 : 5-di-(6'-hydroxyveratrylideneacetic acid), decomp. 245—255°. When heated at >360°/3 mm., this gives 2 : 5-di-2'-hydroxy-4' : 5'-dimethoxystyryl-*p*-xylylene, decomp. 55—60°, unstable in presence of H₂O. When H₂SO₄ and then pure iso-C₅H₁₁·O·NO are added to (I) in dioxan and the resulting solution is poured into aq. NaH₂PO₂ containing Cu powder at 45—55° and then warmed to 80°, 59% of 9 : 10-dimethyl-1 : 2 : 5 : 6-di-(3' : 4'-dimethoxybenz)anthracene-4 : 8-dicarboxylic acid, decomp. 315—317° (corr.), is obtained; other conditions fail. Heating with basic Cu carbonate in quinaldine at 250° then gives 9 : 10-dimethyl-1 : 2 : 5 : 6-di-(3' : 4'-dimethoxybenz)anthracene, m.p. 137—138° (corr.); most attempts to hydrolyse the OMe gave dark products, but those obtained by HBr

or HI gave with Ac_2O a little of the 3' : 4' : 3'' : 4''-(OAc)₄-derivative, decomp. 300—350°. R. S. C.

Hydrogen bonding by S-H. VII. Aryl mercaptans. M. J. COPLEY, C. S. MARVEL, and E. GINSBERG (J. Amer. Chem. Soc., 1939, 61, 3161—3162; cf. A., 1939, I, 518).—Absence of heat changes on mixing shows that $n\text{-C}_6\text{H}_{15}\text{-SH}$ forms no compound with NMe_2Ac , Et_2O , COMe_2 , or C_6H_6 . PhSH forms a 1 : 1 compound with NMe_2Ac , Et_2O , or COMe_2 due to a $\text{H}\leftarrow\text{N}$ or $\text{H}\leftarrow\text{O}$ linking. Such linkings are formed whenever a covalent H linking is sufficiently stabilised. Comparison of the b.p. of MeSH , Me_2S , PhSH , and PhSMe shows absence of association of the mercaptans, confirming the view that there is little tendency towards formation of $\text{S}\rightarrow\text{H}$ linkings.

R. S. C.

Manufacture of 4 : 4'-diaminodiphenylsulphoxides.—See B., 1939, 1213.

Sulphonation with sulphites. IV. Oxidation of sodium sulphite in presence of β -naphthol-sulphonic acids. S. V. BOGDANOV (J. Gen. Chem. Russ., 1939, 9, 1145—1147).—Aq. Na β -naphthol-4- or -7-sulphonate or -3 : 6-disulphonate heated at 85° with Na_2SO_3 and MnO_2 yields, respectively, Na β -naphthol-1 : 4- or -1 : 7-di- or -1 : 3 : 6-tri-sulphonate.

R. T.

d- and l- α -Phenylallyl alcohols and their reactions. D. I. DUVEEN and J. KENYON (J.C.S., 1939, 1697—1701; cf. A., 1937, II, 146; 1939, II, 45).—Partly an account of work previously reviewed (A., 1938, II, 275). *dl*- α -Phenylallyl alcohol (I) and $\text{o-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$ at 50° give the *dl*-*H* phthalate (II), m.p. 73—74° (cf. Kamai, A., 1931, 1393), which affords the *quinidine* salts, m.p. 161—163° (decomp.), $[\alpha]_{589.3}^{20} +106.8^\circ$ in CHCl_3 , and m.p. 124° (decomp.), $[\alpha]_{589.3}^{20} +128.9^\circ$ in CHCl_3 , of the *d*- (III), $[\alpha]_{589.3}^{20} -42.3^\circ$ in CS_2 , and *l*-*H* phthalate (IV), $[\alpha]_{589.3}^{20} -14^\circ$ in EtOH , $+42.6^\circ$ in CS_2 (other vals. of α given), respectively, and thence by aq. KOH-EtOH *d*-, b.p. 107°/16 mm., $[\alpha]_{589.3}^{20} +12.1^\circ$ in CS_2 , and *l*- α -phenylallyl alcohol (V), b.p. 106°/16 mm., $\alpha_{589.3}^{18} -20.08^\circ$ (l, 2), respectively. (IV) in a closed vessel after 4 months gives cinnamyl *H* phthalate, m.p. 95—97° (lit. 88—89°), but (II) appears to be permanently stable. (V) and $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at room temp. overnight, then at 40° for 1 hr., give *l*- α -phenylallyl acetate, b.p. 111°/16 mm. (I) similarly, or (I)- Ac_2O at 100° (bath) for 3 hr., gives *dl*- α -phenylallyl acetate, b.p. 114°/19 mm. (no conversion into cinnamyl acetate occurs). (I) and $\text{K-MeI-Et}_2\text{O}$ give *dl*- α -phenylallyl *Me* ether (VI), b.p. 85°/18 mm. Comparison of the reactivities of (I) and some of its esters with those of α -phenyl- γ -methylallyl alcohol and its corresponding esters (*loc. cit.*; cf. Burton, A., 1928, 880) shows that the latter undergo anionotropic changes far more readily than the former; the greater reactivity is ascribed to the influence of the γ -Me. The stability of (I) to dil. H_2SO_4 is confirmed (cf. Burton *et al.*, A., 1928, 634). (II) or (IV) in anhyd. MeOH , distilled slowly, gives $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and (VI). (III) in MeOH in a closed vessel at room temp. for 3 weeks gives mainly the *d*-*H* phthalate of almost unchanged α , and a little (VI). (IV) in EtOH gradually (33 months) gives $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and α -phenylallyl *Et*

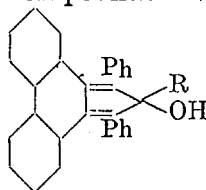
ether, b.p. 90—95°/20 mm. (III) and anhyd. HCO_2H in CS_2 quickly give $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, partly racemised *H* phthalate, and cinnamyl formate, new m.p. 6°, b.p. 132—139°/18 mm. (IV)- AcOH at 100° (bath) afford some $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and cinnamyl acetate.

A. T. P.

Decomposition reactions of aromatic diazo-compounds. IX. Oxidation mechanisms. W. A. WATERS (J.C.S., 1939, 1805—1807).—Benzene-diazoacetate, CaCO_3 , and cyclohexene (I) gradually give some Δ^2 -cyclohexenyl acetate, also formed from PhN_2Cl and (I) in aq. $\text{COMe}_2\text{-NaOAc-CuCl}_2$ (cf. Meerwein *et al.*, A., 1939, II, 262). PhN_2Cl and (I)- $\text{COMe}_2\text{-CaCO}_3$ at 60° give some Δ^2 -cyclohexenyl chloride. Analogous substitution of reactive CH_2 occurs when (I) is oxidised by atm. $\text{O}_2\text{-Os}$, $\text{SeO}_2\text{-AcOH}$, or $\text{Pb(OAc)}_4\text{-AcOH}$. All these reactions may have a common mechanism in which neutral radicals are involved.

A. T. P.

Action of phencyclone on organo-magnesium compounds. V. S. ABRAMOV and P. G. MALSKI (J.



Gen. Chem. Russ., 1939, 9, 1533—1536).—Phencyclone and MgRBr yield phenanthrocylopentadienols: $\text{R} = \text{Ph}$, m.p. 255—257°, *Et*, m.p. 179—180°, *Bu*^a, m.p. 237—239°, CH_2Ph , m.p. 264—265° (hydrate, m.p. 158—159°).

R. T.

Colour reactions of benzaldehyde with sterols and steroids imposed on concentrated sulphuric acid. I. SCHERRER (Helv. Chim. Acta, 1939, 22, 1329—1340).—The colour reactions of the following compounds with $\text{PhCHO} + \text{conc. H}_2\text{SO}_4$ and with conc. H_2SO_4 alone are tabulated: cholesterol, ergosterol, sitosterol, stigmasterol, cholic, glycocholic, and 3-acetoxycholenic acids, calciferol, deoxycorticosterone acetate, androstane-3c : 17c-, -3c : 17t-, -3t : 17c-, and -3t : 17t-diols, androsterone, *cis*- and *trans*-isoandrosterone, dihydro-*c*- and -*t*-testosterone, androstane-3 : 17-dione, Δ^4 -androstene-3 : 17-dione, *cis*- and *trans*-dehydroandrosterone, testosterone, *cis*- and *trans*-testosterone, methyltestosterone, Δ^5 -androstene-3t : 17c- and -3t : 17t-diol, Δ^5 -17-methylandrostene-3t : 17?-diol, progesterone, pregnenolone acetate, β - and α -oestradiol, oestrone, equilin, and oestrin.

H. W.

Configuration of the $\text{C}_{(3)}$ hydroxyl group in sterols precipitable by digitonin. K. GANAPATHI (Current Sci., 1939, 8, 360—361).—The non-precipitability of the 2 : 3-dihydroxycholestane (I) of Marker *et al.* (A., 1939, II, 368) with digitonin is regarded as due to the *epi* (α) configuration of OH at $\text{C}_{(3)}$. The *trans*-configuration of the OH of (I) is regarded as established since oxidation of the cyclic double linking with H_2O_2 (in absence of OsO_4) and hydrolysis of the cyclic oxide yield the same *trans*-glycol, *e.g.*, prep. of 3 : 5 : 6-trihydroxycholestane, m.p. 231°, from cholesterol. Further, if the OH are *cis* (with OH at $\text{C}_{(3)}$ of the *epi*-form), by analogy with the behaviour of *cis*-2 : 3-dihydroxy-*trans*-decahydronaphthalene (*ibid.*, 420), the compound should isomerise on treatment with Ac_2O ; this has not been observed.

H. W.

Colour reactions of sterols and steroids; their importance for the investigation of constitutional problems and hormonal action. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1939, 22, 1309—1328).—The transformation of the two $\text{CH}\cdot\text{OH}$ groups of the androstane-3 : 17-diols into CO and the presence of a single CO in the absence of OH in the ring system (e.g., cholestanone, progesterone) is accompanied by the inhibition of the colour reaction with conc. H_2SO_4 and the more or less pronounced weakening of the furfuraldehyde (I)– H_2SO_4 reaction. The entry of a double linking into the steroid skeleton so restores the colour character that the reaction with H_2SO_4 alone becomes positive (Δ^4 -androstene-3 : 17-dione). This feature is further enhanced when one or both CO groups are reduced. The position of OH is important and pronounced action of *cis-trans* isomerism and other constitutive factors is observed. Replacement of H at C_{17} by Me causes a darkening of the colour. Comparison of the reactions of compounds of the testosterone and dehydroandrosterone groups shows that it is not immaterial in which ring the double linking is located. It appears probable that the introduction of a double linking into the bile acids causes a more pronounced action with (I) + H_2SO_4 and with H_2SO_4 alone; it certainly causes a change in the nature of the colour. The immediate action of pregnenolone or its acetate proves the marked influence of the presence of a double linking in the sterol ring system; the auxochromic action of OH at $\text{C}_{3\beta}$ is also obvious. H. W.

Œstradiol 17-acylates.—See B., 1939, 1295.

Rearrangement of phenyl allyl ethers. III. Synthesis of α -*o*-anisylpropionic acid. W. M. LAUER and L. I. HANSEN. V. Isomeric ethyl *p*- α - and - γ -propylallyloxybenzoates. W. M. LAUER and R. M. LEEKLEY. VI. Isomeric ethyl *p*- α - and - γ -ethylallyloxybenzoates. W. M. LAUER and H. E. UNGNADE (J. Amer. Chem. Soc., 1939, 61, 3039—3041, 3043—3047, 3047—3049; cf. A., 1936, 1244).—III. *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ (prep. from the chloride by aq. KCN in COMe_2) and boiling KOH – EtOH – H_2O give the acid, m.p. 123—124°, the Et ester of which with NaOEt and $\text{Et}_2\text{C}_2\text{O}_4$ in EtOH give an ester, converted by distillation into CO and *Et*₂ *o*-anisylmalonate, b.p. 162—164°/4.5 mm. With NaOEt – EtOH , followed by MeI , this gives *Et*₂ *o*-anisylmethylmalonate, m.p. 42—43°, b.p. 150—151°/2.6 mm., hydrolysed to the malonic acid, m.p. 148.5—149° (decomp.), which in boiling xylene gives α -*o*-anisylpropionic acid (I), m.p. 101—102° (cf. loc. cit.). *Et*₂ *o*-anisylethylmalonate, m.p. 66—67°, α -*o*-anisylbutyric acid, m.p. 56—57°, b.p. 165—166°/10 mm., Et *p*-anisylacetate, b.p. 148—150°/14.5 mm., *Et*₂ *p*-anisyl-, b.p. 161—162°/3 mm., and *p*-anisylmethylmalonate, b.p. 160—161°/3.5 mm. (derived acid, m.p. 149.5—150°), and α -*p*-anisylpropionic acid, m.p. 56—57°, are also prepared. Catalytic hydrogenation of *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ is difficult, but reduction of the derived acid by Na – Hg in aq. NaOH yields β -*o*-anisyl-*n*-butyric acid, m.p. 49—50°, b.p. 172°/9 mm., the Et ester, b.p. 153—154°/9 mm., of which with MgPhBr gives an oily carbinol, dehydrated by

boiling Ac_2O to an oily ethylene derivative, which is oxidised by CrO_3 to (I).

V. Some expected abnormal rearrangements are demonstrated (cf. Hurd *et al.*, A., 1939, II, 137). *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ (II), $\text{CH}_2\cdot\text{CH}\cdot\text{CHPr}^a\text{Cl}$, and K_2CO_3 in boiling COMe_2 give mixed esters, hydrolysed to *p*- γ - (III), m.p. 138—139°, and *p*- α -propylallyloxybenzoic acid (IV), dimorphic, m.p. 35—38° and 76—77° (with O_3 yields CH_2O). When boiled at 40 mm. (b.p. rises from 220° to 246°), the *Et* ester, b.p. 95—97°/0.5 mm., of (IV) gives the normal rearrangement product, viz., *Et* 4-hydroxy-3- Δ^{β} -*n*-hexenylbenzoate, m.p. 75—76.5°, which with NaOMe and Me_2SO_4 in boiling MeOH gives 4-methoxy-3- Δ^{β} -*n*-hexenylbenzoic acid, m.p. 107—108° [with O_3 gives Pr^aCHO ; unaffected by $\text{Hg}(\text{OAc})_2$; hydrogenated ($\text{Pd}-\text{CaCO}_3$) to 4-methoxy-3-*n*-hexylbenzoic acid, m.p. 113.5—114°], and with 66% KOH at 155—150° gives 4-hydroxy-3- Δ^{α} -*n*-hexenylbenzoic acid, m.p. 134—135° [gives a ppt. with $\text{Hg}(\text{OAc})_2$]. The *Et* ester (V), b.p. 115—116°/0.2 mm., of (III) is obtained from (II) by $\text{CHPr}^a\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ and K_2CO_3 in boiling COMe_2 and is hydrolysed by 25% KOH – MeOH to (III), m.p. 139.5—140.5°, which is reduced to *p*-*n*-hexyloxybenzoic acid, m.p. 105.5—107°, obtained also from (II) by NaOEt and *n*- $\text{C}_6\text{H}_{13}\text{Br}$ and subsequent hydrolysis. When boiled at 40 mm. (b.p. rises from 213° to 241°), (V) gives mixed esters (A) (O_3 gives CH_2O and EtCHO), converted by NaOEt – Me_2SO_4 into 4-methoxy-3- α -propylallyl- (VI), m.p. 142.5—143.5°, and 4-methoxy-3- α -methyl- Δ^{β} -*n*-pentenylbenzoic acid (VII), m.p. 113—114°, both without action on $\text{Hg}(\text{OAc})_2$. (VII) is derived from the abnormal rearrangement product. Ozonolysis of (VII) gives *EtCHO and hydrogenation gives 4-methoxy-3- α -methyl-*n*-amylbenzoic acid, m.p. 125—126°. (VI) gives similarly CH_2O and 4-methoxy-3- α -ethyl-*n*-butylbenzoic acid, m.p. 145—146°, respectively. Alkaline hydrolysis of (A) gives 4-hydroxy-3- α -propylallylbenzoic acid, m.p. 133—134°; the more sol. isomeride could not be isolated.*

VI. Two further cases of abnormal rearrangement are reported. $\text{CH}_2\cdot\text{CH}\cdot\text{CHEtCl}$, (II), and K_2CO_3 in COMe_2 give esters, hydrolysed to *p*- α - (VIII), m.p. 108—109° (O_3 gives CH_2O), and *p*- γ -ethylallyloxybenzoic acid (IX), m.p. 156.5—157.5° (157—158°). The *Et* ester (prep. from the Ag salt) of (VIII) at 200—236°/40 mm. gives a product, m.p. 101—102° [with 8.6% of $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$ (X)], converted as above into 4-methoxy-3- Δ^{β} -*n*-pentenylbenzoic acid, m.p. 117—117.5°, unaffected by $\text{Hg}(\text{OAc})_2$ and with O_3 in EtBr at 0° giving *EtCHO*. The *Et* ester, f.p. 34.1°, b.p. 108—109°/0.1 mm., obtained from (II) by $\text{CHEt}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ and K_2CO_3 in COMe_2 and hydrolysed to (IX), is pyrolysed at 195—233°/40 mm. to mixed phenols [and 13.3% of (X)], which yield 4-methoxy-3- α -ethylallylbenzoic acid, m.p. 164.5—165.5° (with O_3 gives CH_2O), and the impure α -methyl- Δ^{β} -butenyl isomeride (with O_3 gives MeCHO and CH_2O). With H_2 – PtO_2 in MeOH , (IX) gives *p*-*n*- $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 123—124°, and with O_3 in EtBr – EtOAc gives *EtCHO*. $\text{CHMe}\cdot\text{CH}\cdot\text{CHMeCl}$, (II), and K_2CO_3 in COMe_2 give *Et* *p*- α -dimethylallyloxybenzoate, b.p. 108—114°/0.1 mm. (corresponding acid, m.p. 131—132°; O_3 gives MeCHO), pyrolysed at 208—223°/40 mm. to (X) (58.5%), *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and mixed

esters, yielding mixed OMe-acids, which with O_3 give MeCHO and a little CH_2O . R. S. C.

Ozonisation of cinnamic acid, sodium cinnamate, ethyl cinnamate, and styrene. E. BRINER and A. GELBERT (Helv. Chim. Acta, 1939, 22, 1483—1490).—Quant. ozonisation of $CHPh:CH:CO_2H$ in MeOH gives a normal ozonide which suffers normal scission into BzOH and $CHO \cdot CO_2H$. $CHPh:CH:CO_2Et$ in CCl_4 is normally ozonised and fission gives mainly PhCHO and $EtHC_2O_4$ with some BzOH and $CHO \cdot CO_2Et$. As is frequently the case, in H_2O $CHPh:CH:CO_2Na$ gives much CO_2 , indicating extensive decomp. of the ozonide. $CHPh:CH_2$ in CCl_4 yields a normal ozonide which affords PhCHO and HCO_2H . Polymerised styrene is ozonised with increasing difficulty as its degree of polymerisation increases. H. W.

Ethers of *p*-hydroxybenzoic acid as derivatives for identification of alkyl halides. W. M. LAUER, P. A. SANDERS, R. M. LEEKLEY, and H. E. UNGNADE (J. Amer. Chem. Soc., 1939, 61, 3050).—Alkyl halides are identified by interaction with $p-OH \cdot C_6H_4 \cdot CO_2Et$ and NaOEt in EtOH and subsequent hydrolysis (KOH-EtOH) to $p-OR \cdot C_6H_4 \cdot CO_2H$. Allylic rearrangements occur in some cases. M.p. of 25 such ethers are listed. *p*-isobutoxybenzoic acid melts at 140—141°. R. S. C.

3-Hydroxy- Δ^5 - α -tiocholenic acid and derivatives.—See B., 1939, 1294.

cycloHexenyl-, cyclohexylidene-, and 1-hydroxycyclohexyl-acetaldehyde.—See B., 1939, 1212.

Alleged geometrical isomerism in certain anils, and dipole moment of phenanthridine.—See A., 1939, I, 598.

Functional aptitude of the methyl group. V. Nitro- and dinitro-toluenes. L. CHARDONNENS and P. HEINRICH (Helv. Chim. Acta, 1939, 22, 1471—1482).— $o-C_6H_4Me \cdot NO_2$ and 1:2:3- $C_6H_3Me(NO_2)_2$ do not appear to condense with $p-NMe_2 \cdot C_6H_4 \cdot NO$ (I), PhCHO, or $p-NMe_2 \cdot C_6H_4 \cdot CHO$ (II), whereas poor yields of condensation products are derived from $p-C_6H_4Me \cdot NO_2$. 1:2:4- $C_6H_3Me(NO_2)_2$ (III) is the most reactive of the dinitrotoluenes. $p-C_6H_4Me \cdot NO_2$ and (I) in boiling EtOH containing anhyd. Na_2CO_3 give *p*-nitrobenzal-*p*'-dimethylaminoanil, m.p. 219°, in 1.5% yield. With PhCHO and (II) in presence of piperidine at 175—185° $p-C_6H_4Me \cdot NO_2$ affords *p*-nitrostilbene, m.p. 155.5°, and 4-nitro-4'-dimethylaminostilbene, m.p. 250°, in 3.5% and 22% yield, respectively. (III), (I), and anhyd. Na_2CO_3 in boiling EtOH yield a mixture of 2:4-dinitrobenzal-4'-dimethylaminoanil, m.p. 209—210°, and the corresponding nitrone (IV), m.p. 194°. In boiling EtOH containing Na_2CO_3 in presence or absence of (I), (IV) is mainly transformed into 2:4-dinitrobenz-4'-dimethylaminanilide, m.p. 238° (decomp.). 2:6-Dinitro-4'-dimethylaminostilbene, m.p. 139°, is obtained in 55% yield from 1:2:6- $C_6H_3Me(NO_2)_2$ (V), (II), and piperidine at 150—160°. 2:6-Dinitrobenzal-4'-dimethylaminoanil, m.p. 150°, is formed in ~1% yield from (I), (V), and anhyd. Na_2CO_3 in boiling EtOH. The following appear new: 2:5-dinitrostilbene, m.p. 149.5° [dibromide, m.p. 220—222° (decomp.)]; 2:5-

dinitro-4'-dimethylaminostilbene, m.p. 168°; 3:4-dinitrobenzal-4'-dimethylaminoanil, m.p. 186—188° (accompanying by an unidentified substance, m.p. 220°), hydrolysed (15% HCl) to 3:4-dinitrobenzaldehyde, m.p. 62.5° (phenylhydrazone, m.p. 184—186°).

H. W.

Synthesis of substances related to the sterols. XXVIII. (SIR) R. ROBINSON and J. M. C. THOMPSON (J.C.S., 1939, 1739—1742; cf. Chuang *et al.*, A., 1939, II, 326).—1- $C_{10}H_7 \cdot [CH_2]_2 \cdot COCl$ and Et_2 sodioacetylsuccinate or Et_2 sodio- α -acetylglutarate (I) give products hydrolysed by aq. KOH-EtOH at room temp., then 2N-NaOH at 100° (bath), to γ -keto- ζ -1-naphthylheptoic acid, m.p. 123—124° [purified through the Me ester (II), b.p. 193—198°/0.4 mm.; semicarbazone, sinters with decomp. at ~170°], or δ -keto- η -1-naphthyl-octoic acid, m.p. 66—67° [Me ester (III), b.p. 200—205°/0.4 mm.; semicarbazone, sinters at ~148°], respectively. The use of 1- $C_{10}H_7 \cdot [CH_2]_2 \cdot CHMe \cdot COCl$ in the above reactions gives no keto-acid (cf. Chuang, *loc. cit.*). (II) and NaOEt (EtOH-free) in Et_2O at room temp. (20 hr.) and then at the b.p. give a syrup, converted by P_2O_5 in boiling moist C_6H_6 into 3'-keto-3:4-dihydro-1:2-cyclopentenophenanthrene, new m.p. 212—213°. (III) and NaOEt in Et_2O similarly give 2- β -1'-naphthylethylcyclohexane-1:3-dione, m.p. 199—200°, converted by P_2O_5 in very damp C_6H_6 [as also is (III) directly] into 3-keto-1:2:3:4:5:6-hexahydrochrysene, m.p. 154—156° [2:4-dinitrophenylhydrazone, m.p. 284° (decomp.)]. γ -*m*-Anisylbutyryl chloride and (I) in C_6H_6 - Et_2O , and hydrolysis of the product with aq. KOH-EtOH, leads to Me δ -keto- η -*m*-anisyl-octoate, b.p. 182—188°/0.25 mm. (42% yield; cf. A., 1936, 989). γ -6-Methoxy-3:4-dihydro-1-naphthylbutyric acid, m.p. 79° (cf. A., 1937, II, 196; Chuang *et al.*, *ibid.*, 294), and S give γ -6-methoxy-1-naphthylbutyric acid. Its chloride and (I) afford a product, hydrolysed by aq. KOH-EtOH at room temp., then 2N-NaOH at 100° (bath), to an acid, methylated (CH_2N_2) to Me δ -keto- η -(6'-methoxy-1'-naphthyl)-octoate, which with NaOEt gives 2- β -6'-methoxy-1'-naphthylethylcyclohexane-1:3-dione, m.p. 170—172°. The latter and P_2O_5 in very damp C_6H_6 give 3-keto-10-methoxy-1:2:3:4:5:6-hexahydrochrysene, m.p. 177—178° [2:4-dinitrophenylhydrazone, m.p. 284° (decomp.)], is crimson, characteristic of $\alpha\beta$ -unsaturated ketones [3 H_2 absorbed (AcOH-Adams' PtO_2) to give a (?)methoxyoctahydrochrysene], converted by Na in boiling EtOH into 3-hydroxy-10-methoxy(or ethoxy)-1:2:3:4:5:6:15:16-octahydrochrysene [p-nitrobenzoate, m.p. 218—219° (softens from 214°)].

A. T. P.

Steroids. II. Isolation of a new androstan-3(β)-ol-7-one and of allopregnan-3(β)-ol-20-one from the urine of pregnant mares. R. D. H. HEARD and A. F. MCKAY (J. Biol. Chem., 1939, 131, 371—379).—The non-phenolic neutral extract of the urine of pregnant mares is shaken with 70% EtOH (I) and light petroleum. The product from (I) gives with Girard's reagent P (A., 1936, 1397) in AcOH, followed by hydrolysis, a ketonic fraction, and this, through the K phthalates, a OH-ketonic fraction, which is distilled, yielding fractions of b.p. <115°, 115—140°, and 140—195° (II) (all air-bath temp./~0.01 mm.).

Purification of (II) through the digitonide and the benzoate, m.p. 206—208°, gives *androstan-3(β)-ol-2-one* (III), m.p. 187—187.5°, $[\alpha]_D^{25} -160^\circ$ in dioxan [oxime, m.p. 194—195° (decomp.)], oxidised to the 3:7-diketone, m.p. 157—158°, which is reduced (Zn-Hg in HCl) to androstane (with no evidence of the formation of an androstanol; cf. Reichstein, A., 1936, 1382). With the Zimmermann reagent, (III) slowly develops a feebly reddish-brown colour: the CO is probably in the 6-, 7-, or 12-position. Another OH-ketonic fraction, b.p. 170—210°/0.01 mm., yielded *allopregnan-3(β)-ol-20-one* (cf. Marker *et al.*, A., 1938, II, 369). E. W. W.

Sterols. LXXV. Cholesterol derivatives.

R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 3022—3024).— H_2 -PtO₂ at 25°/3 atm. reduces 7-ketocholesteryl chloride in Et₂O to 7-ketocholesteryl chloride, m.p. 136—138° (cf. A., 1937, II, 250) (oxime, m.p. 152—154°). 7-Keto-Δ^{5:6}-cholesten-3(β)-yl acetate in Et₂O with H_2 -PtO₂ gives the acetate (I), m.p. 147—148°, of 7-ketocholestan-3(β)-ol, double m.p. 128—130° and 157—159° (oxime, m.p. 232—233°), but with H_2 -PtO₂ in AcOH gives an oily acetate, hydrolysed to *cholestane-3(β):7(α)-diol*, m.p. 164—166°, which is also obtained from (I) by Al(OPrⁱ)₃-PrⁱOH, and with CrO₃ gives *cholestane-3:7-dione*, m.p. 186—187°. 7-Hydroxycholesteryl chloride and Na-C₅H₁₁-OH give Δ^{5:6}-cholesten-7-ol, m.p. 105—106° (benzoate, m.p. 145—147°), which with H_2 -PtO₂ in abs. EtOH-Et₂O gives *cholestan-7-ol* and when treated successively with Br, CrO₃, and Zn dust gives Δ^{5:6}-cholesten-7-one, m.p. 125—126°. SeO₂ in C₆H₆-98% AcOH (cf. A., 1938, II, 276) oxidises cholesteryl acetate to 4-hydroxycholesteryl acetate, dimorphic, m.p. 163—165° and 189—191°. R. S. C.

Steroid ketones.—See B., 1939, 1293, 1294, 1295.

Reaction between dihydroanthracene and benzoquinone. E. I. PROKOPETZ and A. V. PAVLENKO (J. Gen. Chem. Russ., 1939, 9, 1468—1469).—9:10-Dihydroanthracene (I) and *p*-benzoquinone (II) at the b.p. yield anthracene (III) and quinol (IV). (II) and (IV) yield quinhydrone (V). (III) and (II) or (V) afford a condensation product. R. T.

Constitution and synthesis of vitamin-K₁. D. W. MACCORQUODALE, L. C. CHENEY, S. B. BINKLEY, W. F. HOLCOMB, R. W. MCKEE, S. A. THAYER, and E. A. DOISEY (J. Biol. Chem., 1939, 131, 357—370).—Largely an account of work already reported (A., 1939, II, 433, 513). 2:3-C₁₀H₆Me₂ gives 2-methyl-3-bromomethylnaphthalene, m.p. 104—105°, which through the nitrile gives 2-methyl-3-naphthylacetic acid, m.p. 200—201°, oxidised (CrO₃) to 2-methyl-1:4-naphthaquinonyl-3-acetic acid (*loc. cit.*). E. W. W.

Nor-α-phyllquinone (norvitamin-K₁) and similar compounds. P. KARRER, A. GEIGER, A. RÜEGGER, and H. SALOMON (Helv. Chim. Acta, 1939, 22, 1513—1516).—2-C₁₀H₇·[CH₂]₂·MgBr and ζξ-trimethylpentadecan-β-one (I) give 2-γ-hydroxy-γλo-tetramethylhexadecylnaphthalene (II), converted into the corresponding chloride, which with C₅H₅N affords 2-γλo-tetramethyl-Δ^β-hexadecylnaphthalene. This is brominated, oxidised, and debrominated

with partial reduction by Zn dust to 1:4-dihydroxy-2-γλo-tetramethyl-Δ^β-hexadecylnaphthalene, which is oxidised to nor-α-phyllquinone (III). The position of the double linking appears assured by the violet colour with NaOEt although the possibility of non-homogeneity is not excluded. The absorption spectrum of (III) is very closely similar to that of phylloquinone. A modified method consists in the condensation of 2-C₁₀H₇·C(CN)Me with (I) to 2-γ-hydroxy-γλo-tetramethyl-Δ^α-hexadecylnaphthalene, which is reduced to (II). Another method consists in the direct condensation of 2:1:4-C₁₀H₅Me(OH)₂ with dihydrophytyl bromide in presence of a catalyst and oxidation of the condensation product. H. W.

Naphthaquinones of the vitamin-K₁ type of structure. L. F. FIESER, W. P. CAMPBELL, E. M. FRY, and M. D. GATES, jun. (J. Amer. Chem. Soc., 1939, 61, 3216—3222).—A detailed account and extension of work already reported (A., 1939, II, 513). The following is new. 2-Methyl-1:4-naphthaquinone (prep. from 2-C₁₀H₇Me in 29% yield by CrO₃-AcOH at <20° and then 50—60°), m.p. 105—106°, is reduced by SnCl₂-HCl-EtOH or Na₂S₂O₄-EtOH to 2:1:4-C₁₀H₆Me(OH)₂ (I) (diacetate, m.p. 112.5—113°; dibenzoate, m.p. 180—180.5°), which with CH₂PhBr-K₂CO₃-COMe₂-N₂ gives the (CH₂Ph)₂ (72%), m.p. 74.5—75°, and CH₂Ph ether, m.p. 159—160° after darkening, or in air 3-benzyl-2-methyl-1:4-naphthaquinone (II), m.p. 107.5—108°. With isoprene or CH₂Ph·OH and anhyd. H₂C₂O₄ in dioxan at 180°, (I) gives oily 2-methyl-3-γ-methyl-Δ^β-n-butenyl-1:4-naphthaquinone (reduced to the quinol diacetate, m.p. 104.5—105.5°) or (II), respectively, but this type of condensation sometimes fails. 2-Ethyl-1:4-naphthaquinone (prep. from β-C₁₀H₇·COMe by Zn-Hg-HCl-MeOH-C₆H₆ and subsequently CrO₃) gives the quinol, m.p. 144—145° (decomp.; softens at 140°) (diacetate, m.p. 104—105°; dibenzoate, m.p. 164—165°), and 3-cinnamyl-2-ethyl-1:4-naphthaquinone, m.p. 118—118.5° (quinol diacetate, m.p. 123.5—124.5°). 1:4-Naphthaquinone oxide, m.p. 134.5—135.5° (lit. 136°), 2-methyl- (III), m.p. 95.5—96.5° (lit. 102°), 2:6- (IV), m.p. 97—98°, and 2:7-dimethyl-1:4-naphthaquinone oxide, m.p. 91—92°, are described. MgMeCl converts (III) into an oil, which with boiling HCl-EtOH gives a substance, C₁₂H₁₃O₂Cl, m.p. 141.5—142°. The bromohydrin, obtained from (IV) by MgBr₂, with NaOAc in boiling AcOH gives 3-bromo-2:6-dimethyl-1:4-naphthaquinone, m.p. 114—114.5°. Although 2-methyl-3-βγ-dimethyl-Δ^β-n-butenyl-1:4-naphthaquinone is converted by reductive acetylation in C₅H₅N into the quinol diacetate, Zn-Ac₂O-NaOAc gives the substance, m.p. 73—73.5° (*loc. cit.*), of tocopherol type. R. S. C.

Products obtained by saturating Δ³-carene with hydrogen chloride. V. N. KRESTINSKI and S. MALEVSKAJA (J. Appl. Chem. Russ., 1939, 12, 878—885).—Δ³-Carene and HCl give the mono- and dihydrochlorides of dipentene and sylvestrene, showing that HCl has a greater affinity for the [CH₂]₃ ring than for the ethylenic linking. R. T.

Dicyclic structures prohibiting the Walden inversion. Replacement reactions of 1-substituted 1-apocamphanes. P. D. BARTLETT and

L. H. KNOX (J. Amer. Chem. Soc., 1939, **61**, 3184—3192).—Reactions of dicyclic compounds are described which cannot occur with Walden inversion because the C in question is "caged in" so as to be inaccessible to attack in the rear and because the cyclic structure prevents change of configuration. To account for the low reactivities of the chloride and alcohol described below, it is suggested that reactions involving a $\geq C^+$ ion occur only when the three remaining valencies are coplanar. *dl*-Ketopinic acid, prepared in 38.4—42.7% yield from *dl*-camphor-10-sulphonyl chloride by Na_2CO_3 - $KMnO_4$, is reduced by the Wolff-Kishner or, more conveniently, Clemmensen-Martin method to *apocamphane*-1-carboxylic acid, m.p. 217—218°, the chloride of which gives the *amide* (92.1%), m.p. 185°, converted by $NaOMe$ - $MeOH$ - Br into the *urethane* (60.2%), m.p. 93—94°, and thence by KOH -aq. $MeOH$ into 1-aminocamphane (I), m.p. 175° (sealed tube) (*hydrochloride*, discolours at 235—240°, m.p. $>320^\circ$). The *Ac* derivative, m.p. 132°, thereof is more slowly hydrolysed by KOH -aq. $EtOH$ than is NH_4Bu^+Ac or Bu^+CO-NH_2 . $NaNO_2$ - H_2SO_4 (excess) converts (I) in conc., aq. solution into *apocamphan*-1-ol (II) (66.6%), m.p. 161—162° (sealed tube). The *p*-toluenesulphonate, m.p. 93°, of (II) does not react with NaI - $COMe_2$. Replacement of the OH by Cl fails by most methods. $SOCl_2$ and (II) give a sulphite, m.p. 95—98°. HBr gas in Et_2O gives an unstable additive compound, $C_{18}H_{33}O_2Br$, m.p. 83—84°, and PCl_5 in light petroleum (b.p. 20—40°) gives a compound, $C_{18}H_{33}O_2Cl$, m.p. variable, 157° to 168°. The *Bz* derivative, m.p. 112°, of (I) and PCl_5 give a tar. $NOCl$ and (I) in Et_2O at -10° give N_2 and 45% of 1-chloroapocamphane, m.p. 154—156°, hydrolysis of which by 30% KOH in hot 80% $EtOH$ or hot $AgNO_3$ - $EtOH$ is exceedingly slow or negligible; it gives no Mg derivative. Bornyl chloride reacts readily with hot $AgNO_3$ - $EtOH$. CEt_2Bu^+OH , b.p. 118—119.6°/160 mm., and dry HCl at 0° readily give γ -chloro- β -dimethyl- γ -ethyl-*n*-pentane, b.p. 53—54°/6 mm., 80.6—81°/150 mm., which reacts readily with 80% $EtOH$ at 25° , as do also Bu^+Cl and CMe_2EtCl . R. S. C.

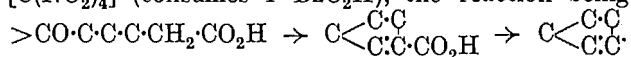
Triterpenes. LI. Transformation of betulin into lupeol. L. RUZICKA and M. BRENNER (Helv. Chim. Acta, 1939, **22**, 1523—1528).—Oxidation of betulin monoacetate with CrO_3 in $AcOH$ followed by treatment of the product with C_5H_5N and $(CH_2CO)_2O$ gives *acetylbetulin aldehyde*, m.p. 199—200° (vac.) on block preheated to 160° and then very slowly heated, $[\alpha]_D +30.3^\circ$ (all $[\alpha]$ in $CHCl_3$), which is converted by $NH_2CO-NH-NH_2$, $AcOH$ into the *semicarbazone* (I), m.p. between 270° and 280° (vac.) according to the rate of heating, and an unidentified compound, m.p. 291—294° on block preheated to 210°. Na in $EtOH$ at 180° converts (I) into deoxybetulin (II), m.p. 212.5—214.5°, $[\alpha]_D +27.2^\circ$, the identity of which with lupeol is further established by the prep. of the benzoate, m.p. 268—271°, $[\alpha]_D +60.9^\circ$, and acetate, m.p. 215—217°, $[\alpha]_D +40.7^\circ$ in $CHCl_3$. (II) is oxidised by Kiliani's mixture to deoxybetulone [lupeone], m.p. 168—170.5°, $[\alpha]_D +60.8^\circ$ [oxime, m.p. 268—273° (decomp.)]. All m.p. are corr. The lupeol type can therefore be added to the three fundamental types of triterpenes, viz., squalene and α - and β -amyrin. H. W.

Saponins and sapogenins. XIV. So-called pyridazines of steroid diones. C. R. NOLLER (J. Amer. Chem. Soc., 1939, **61**, 2976—2977).—The so-called "pyridazines" from chlorogenin and cholestane-3:6-dione are multimol. (cryoscopy in C_6H_6), the mol. wt. of different preps. varying widely in spite of similar m.p. (cf. Marker *et al.*, A., 1939, II, 261, 277).

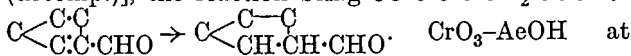
R. S. C.

Lactonisation of dihydro-*l*-abiatic and -*l*-pimaric acids. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1939, **61**, 3197—3199).—The lactone, m.p. 127—129° (structure suggested), is obtained from dihydro-*l*-pimaric acid, m.p. 144—146°, $[\alpha]_D^{20} +35^\circ$, or dihydroabiatic acid, $[\alpha]_D +108^\circ$. With 10% KOH - Bu^+OH , or with 88% KOH at 200° , it gives hydroxy-tetrahydroabiatic acid, m.p. 164—165° (evolution of H_2O and lactonisation), the *Me* ester, m.p. 50—51°, $[\alpha]_D^{20} +21^\circ$ in abs. $EtOH$, b.p. 175—180°/2 mm., of which is stable to $KMnO_4$ in $COMe_2$ or aq. alkali, but gives no acetate or benzoate, even warm $AcOH$ readily converting it into the lactone. R. S. C.

Cerin and friedelin. V. Friedonic acid. N. L. DRAKE and J. K. WOLFE (J. Amer. Chem. Soc., 1939, **61**, 3074—3078).—Friedonic acid (I), prepared (modified method; cf. A., 1936, 1386) by oxidation of friedelin (II), was accompanied, in one experiment only, by an *isomeride*-A, m.p. 126—127°, into which (I) is partly converted by $NaOEt$ - $EtOH$ at room temp. -A is unaffected by cold alkali, with $NaOMe$ - Me_2SO_4 in boiling $MeOH$ gives *Me friedonate* (III), m.p. 157—158° [obtained also from (I) similarly or by CH_2N_2 or from Na friedonate by MeI], and consumes 3.0 mols. of $MgMeI$, giving 0.58 CH_4 . (I) and (III) consume 4.15 and 3.0 mols. of $MgMeI$, giving 1.57 and 0.52 CH_4 , respectively. The structure of -A is unknown, except that the enolisable CO of (III) persists. The CO of (I) is confirmed by an absorption max. ($\log \epsilon$ 1.55) at 2900 Å. (absence of $C:C:CO$). At 250° in N_2 , (I) gives 1 mol. each of CO_2 , H_2O , and *norfriedelene* (IV), $C_{29}H_{48}$, m.p. 228.5—230°, unsaturated $[C(NO_2)_4]$ (consumes 1 BzO_2H), the reaction being



H_2 - PtO_2 reduces (IV) in Et_2O - $EtOAc$ to *norfriedelane*, $C_{29}H_{50}$, m.p. 220—221°, saturated. $KMnO_4$ - $AcOH$ and (IV) give *norfriedonic acid*, $C_{29}H_{48}O_3$, m.p. 215—217° [oxime, m.p. 270.5—273°; *Me* ester, m.p. 166—167° (oxime, m.p. 193—195°; 2:4-dinitrophenylhydrazone, m.p. 233—234°)], reduced by Na - Pr^+OH to *norfriedelolactone* (*loc. cit.*). Boiling $SOCl_2$ converts (I) into a non-cryst. acid chloride, reduced by H_2 - Pd - $BaSO_4$ in xylene at 150° to *norfriedelanylformaldehyde* (V), $C_{30}H_{50}O$, m.p. 222—225° [oxime, m.p. 255—259°; 2:4-dinitrophenylhydrazone, m.p. 312—314° (decomp.)], the reaction being $CO-C-C-C-CH_2 \cdot COCl \rightarrow$



100° oxidises (V) to *norfriedelanylformic acid*, $C_{30}H_{50}O_2$, m.p. 307—308° (*Me* ester, m.p. 230—231.5°). It is concluded that (I) is an ϵ -CO-acid, of which the CO is

highly hindered and that (II) contains $C < \begin{matrix} CH-CO \\ C-CH_2 \end{matrix}$.

R. S. C.

Breakdown products of lignin. P. A. BOBROV and L. A. KOLOTOVA (Compt. rend. Acad. Sci. U.R.S.S.,

1939, 24, 49—51; cf. A., 1938, III, 452).—Reduction of the OH-acids produced by the neutral oxidation of lignin yields AcOH, PrCO_2H , $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and hexoic acid. Alkaline oxidation of lignin yields in addition to the OH-acids a white substance, $\text{C}_8\text{H}_8\text{O}_4$, which gradually darkens through yellow to black, and when dry distilled gives a distinct reaction for furan.

D. F. R.

Lignin and related compounds. XLVI. Action of ozone on isolated lignins. R. M. DORLAND, W. L. HAWKINS, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 2698—2701; cf. A., 1939, II, 516).—Ozonisation of birch HCO_2H -lignin progressively decreases the OMe content and increases the solubility in NaHSO_3 . Alkaline cleavage of the ozonised, sulphonated material gives ~1% of vanillin and acetovanillone. Similar treatment of the AcOH-lignin gives 2·7% of the products.

R. S. C.

Pigment of the seed-husks of *Andropogon sorghum*, Brot. A. V. ZACHAROVA (J. Appl. Chem. Russ., 1939, 12, 1039—1044).—The husks contain Et_2O -sol. 2·2, EtOAc -sol. 2·9, and EtOH -sol. substances 2·1%. The Et_2O -sol. fraction contains a red substance, $\text{C}_{19}\text{H}_{34}\text{O}_2$, m.p. 81—84°, which when heated at 200—225° with KOH yields pyrogallol (I), and other products, not identified. The EtOAc fraction yielded a substance, $\text{C}_{16}\text{H}_{16}\text{O}_6$, decomp. 300°, from which protocatechuic acid (II), BzOH , (I), and a ketone, m.p. 56—57° (semicarbazone, m.p. 155—156°), were obtained by fusion with KOH. The product isolated from the EtOH fraction melted at 117·5—119°, and gave (I), (II), BzOH , and an aldehyde by fusion with KOH. It is concluded that the husks contain a no. of related pigments, which form lakes with Cu, Ni, Zn, Fe, and Al.

R. T.

Osage orange pigments. II. Isolation of a new pigment, pomiferin. M. L. WOLFROM, F. L. BENTON, A. S. GREGORY, W. W. HESS, J. E. MAHAN, and P. W. MORGAN (J. Amer. Chem. Soc., 1939, 61, 2832—2836).—Osajin (I), extracted from the osage orange, is accompanied by *pomiferin* (II), $\text{C}_{25}\text{H}_{24}\text{O}_6$, m.p. 200·5°, with which it was, in part, previously (A., 1938, II, 239) confused. The diacetate of (I) has m.p. 164°. (II) gives a *di-p-toluenesulphonate*, m.p. 148° [previously ascribed to the (I) series], *diacetate* (prep. by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 0°), m.p. 134·5° (green FeCl_3 colour), *triacetate* (prep. by boiling $\text{Ac}_2\text{O}\cdot\text{NaOAc}$), m.p. 154°, Me_2 (prep. by $\text{Me}_2\text{SO}_4\cdot\text{KOH}\cdot\text{MeOH}$ at 0° to room temp.), m.p. 132° (*acetate*, m.p. 128—129°), and Me_3 *ether* (prep. by hot $\text{Me}_2\text{SO}_4\cdot 50\% \text{ KOH}\cdot\text{COME}_2$), m.p. 139·5°, and has an absorption max. at 2750 Å. The absorption max. of (I) is at 2730 Å. Hot $\text{H}_2\text{SO}_4\cdot\text{AcOH}$ isomerises (I) and (II) to *isoosajin*, m.p. 285° (decomp.; block), and *isopomiferin*, m.p. 265° (decomp.; block), having absorption max. at 2660 and 2680 Å, respectively.

R. S. C.

Phoenicopterin from flamingo fat.—See A., 1939, III, 1062.

Reaction of tetrahydrofuran and 2:5-dimethyltetrahydrofuran with acyl halides. J. B. CLOKE and F. J. PILGRIM (J. Amer. Chem. Soc., 1939, 61, 2667—2669).—Prep. of furan from furoic acid and a little CuO in quinoline at 225° and thence of tetra-

hydrofuran (I) by H_2 -Raney Ni at 55—100 atm. is described. When boiled with AcCl , (I) gives 42—50% of $\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{OAc}$ (II), b.p. 90—91°/20 mm., with considerable amounts of δ -8'-chlorobutoxybutyl acetate, b.p. 165—167°/24 mm., and a little δ -8'-8'-chlorobutoxybutoxybutyl acetate, b.p. 175—178°/10 mm. Addition of a trace of ZnCl_2 leads to 76% of (II), but addition of AlCl_3 leads to very little (II). Use of other acyl halides affords δ -chlorobutyl propionate, b.p. 101·5—102·5°/20 mm., *n*-butyrate, b.p. 112·5—113·5°/20 mm., and benzoate, b.p. 140—142·5°/4 mm., and impure δ -bromobutyl acetate, b.p. 89·5—92°/15 mm., and benzoate, b.p. 155—157°/9 mm. 2:5-Dimethyltetrahydrofuran (prep. described), b.p. 89—91°, AcCl , and a little ZnCl_2 gives ϵ -chloro- β -acetoxy-*n*-hexane, b.p. 94—95°/20 mm., but AcBr gives a mixture. With $\text{HCl}\cdot\text{MeOH}$ at 40°, (II) gives 80% of $\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{OH}$.

R. S. C.

sec.-2-Furfurylamines. J. E. ZANETTI and J. T. BASHOUR (J. Amer. Chem. Soc., 1939, 61, 3133—3134).—2-Furfuryl bromide (1 mol.), the appropriate amine, and KOH in Et_2O give 50—65% of *N*-2-furfurylmethyl-, b.p. 149—149·3°/761 mm., ~50—57°/16·5—18 mm. (hydrochloride, m.p. 144—146°), -ethyl-, b.p. 165—167°/761 mm., 63—65°/17—18 mm. (hydrochloride, m.p. 127—128°), -*n*-butyl-, b.p. 198—200°/768 mm., 92—95°/16—18 mm. (hydrochloride, m.p. 189—191°), and -*n*-amyl-amine, b.p. 214—216°/756 mm., 108—111°/16—18 mm. (hydrochloride, m.p. 185—188°), and *N*-2-furfurylaniline, b.p. 109—110°/0·5 mm. [hydrochloride, m.p. 150—151° (decomp.)], with varying amounts of (?) *tert.* amines.

R. S. C.

$\alpha\delta$ -Diphenyl- β -mesityl- $\alpha\delta$ -diketones. R. E. LUTZ and C. J. KIBLER (J. Amer. Chem. Soc., 1939, 61, 3007—3010).—A β -mesityl group in $(\text{CH}_2\text{Bz})_2$ increases the ease of furan formation to such an extent that the mesityl-diketone cannot be isolated. The furan formed is not sterically hindered. Addition of $(\text{CHBz})_2$ to Mg mesityl bromide (3 mols.) in Et_2O gives the dienolate, $\text{OMgBr}\cdot\text{CPh}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_2\text{Me}_3)\cdot\text{CPh}\cdot\text{OMgBr}$, converted by dil. HCl into 2:5-diphenyl-3-mesitylfuran (I) (65%; sole product, even in presence of I), m.p. 157·5—158°, which with conc. $\text{HNO}_3\cdot\text{AcOH}$ at 10° gives *cis*- $\alpha\delta$ -diketo- $\alpha\delta$ -diphenyl- β -mesityl- Δ^8 -butene (II) (90%), m.p. 98·5—99°, stable to light in EtOH or CHCl_3 -I. Zn dust in AcOH , $\text{Na}_2\text{S}_2\text{O}_4$ -70% EtOH , or H_2 - PtO_2 in 70% EtOH reduces (II) to (I). $\text{HCl}\cdot\text{AcOH}$ at room temp. converts (II) into 4-chloro-2:5-diphenyl-3-mesitylfuran, m.p. 102·5—103·5°, also obtained in poor yield from (I) by PCl_5 at 100° or 120°, reduced by Zn dust- AcOH to (I), and oxidised ($\text{AcOH}\cdot\text{HNO}_3$) to *cis*- γ -chloro- $\alpha\delta$ -diketo- $\alpha\delta$ -diphenyl- β -mesityl- Δ^8 -butene, m.p. 127·5—128°. $\text{HBr}\cdot\text{AcOH}$ and (II) at room temp. or PBr_5 and (I) at room temp. give 65% of 4-bromo-2:5-diphenyl-3-mesitylfuran, m.p. 126—127°, also obtained from (II) by PBr_5 at 0° and converted by $\text{HNO}_3\cdot\text{AcOH}$ into *cis*- γ -bromo- $\alpha\delta$ -diketo- $\alpha\delta$ -diphenyl- β -mesityl- Δ^8 -butene (95% yield), m.p. 103—104·5°, unstable in light [$\text{Zn}\cdot\text{AcOH}$ gives (I)]. Ac_2O and a little H_2SO_4 convert (II) into 4-acetoxy-2:5-diphenyl-3-mesitylfuran, m.p. 124·5—126·5°. M.p. are corr.

R. S. C.

β -Phenyl- $\alpha\delta$ -dimesityl- $\alpha\delta$ -diketones. R. E. LUTZ and C. J. KIBLER (J. Amer. Chem. Soc., 1939, **61**, 3010—3012).—2 : 4 : 6- $C_6H_2Me_3\cdot CO\cdot CH_2\cdot CHPh\cdot CO\cdot C_6H_2Me_3$ 2 : 4 : 6 (I) is not cyclised by $Ac_2O\cdot H_2SO_4$, but with HI (d 1.7) at 145—150° or, better, when boiled for 30 hr. with AcOH containing a little H_2O and saturated with HCl gives 3-phenyl-2 : 5-dimesitylfuran, m.p. 104—105.5°, converted by $HNO_3\cdot AcOH$ at 10° into the (? 4-) NO_2 -derivative, m.p. 164—165°. When (2 : 4 : 6- $C_6H_2Me_3\cdot CO\cdot CH_2$)₂ is added to MgPhBr (3 mols.) in Et_2O and the product is then treated with I or $p\text{-}O\text{-}C_6H_4\text{-}O$ in EtOH, 46% of $\alpha\delta$ -diketo- β -phenyl- $\alpha\delta$ -dimesityl- Δ^8 -butene (II), m.p. 109—110°, is formed, proving that prep. of (I) (Lutz *et al.*, A., 1934, 895) proceeds by way of the dienolate. Zn-dust-AcOH reduces (II) to (I). Attempts to prepare an acetoxyfuran from (II) failed. M.p. are corr. R. S. C.

Derivatives of coumaran. VI. Reduction of 1-acetobenzfuran and its derivatives. R. L. SHRINER and J. ANDERSON (J. Amer. Chem. Soc., 1939, **61**, 2705—2708; cf. A., 1939, II, 518).—1-Acetobenzfuran (I) with $H_2\text{-}PtO_2\text{-}Pt$ in abs. EtOH at 2—3 atm. gives 1- α -hydroxyethylbenzfuran (II), m.p. 41° (Stoermer *et al.*, A., 1903, i, 846, m.p. 37°), b.p. 147°/19 mm. [phenylurethane, m.p. 102—103° (*loc. cit.*, 126°)]. With H_2 -Raney Ni in EtOH at 2—3 atm., (I) or (II) gives 1- α -hydroxyethylcoumaran (III), b.p. 145°/20 mm. [phenylurethane, m.p. 115—116° (*loc. cit.*, 73°)]. In presence of Pt-C, hydrogenation gives mixtures of (II), (III), and the corresponding Et compounds. Hydrogenation of (I) thus occurs primarily by 1 : 2-addition. With a large excess of Na-Hg, (I) gives 1-acetylcoumaran [semicarbazone, m.p. 168—169° (lit. 192°)], obtained also from (III) by CrO_3 . ω -Bromo-1-acetobenzfuran [prep. from (I) described], m.p. 90—91°, and NaOAc in HCl-EtOH- H_2O give ω -acetoxy-1-acetobenzfuran, m.p. 86—87°, reduction of which by H_2 -catalysts or Na-Hg-AcOH results in cleavage to AcOH and (I) or its reduction products. However, $COPh\cdot CH_2\cdot OAc$ and $H_2\text{-}PtO_2$ in EtOH at 2—3 atm. give mainly α -phenylethylene glycol β -acetate, b.p. 136—137°/1 mm., with only small amounts of AcOH and $CHPhMe\cdot OH$. R. S. C.

Vitamin-E. XVIII. Condensation of phenols and quinols with allylic alcohols, allylic halides, and conjugated dienes. L. E. SMITH, H. E. UNGNADE, J. R. STEVENS, and C. C. CHRISTMAN (J. Amer. Chem. Soc., 1939, **61**, 2615—2618; cf. A., 1939, II, 518).—Condensation of substituted allyl alcohols with phenols and quinols does not always proceed by way of the dienes, as the latter sometimes give different products. Reaction mechanisms are suggested. 2 : 3 : 5 : 1 : 4- $C_6HMe_3(OH)_2$ (I), $CH_2\text{-}CH\text{-}CH_2\text{-}OH$, and $ZnCl_2$ in C_6H_6 at 200° give 4-hydroxy-1 : 3 : 5 : 6-tetramethylcoumaran, also obtained from $CH_2\text{-}CH\text{-}CH_2Cl$ and (I) at 150°. Similarly, $CH_2\text{-}CH\text{-}CHMe\cdot OH$, (I), and $ZnCl_2$ in C_6H_6 at 200° give 4-hydroxy-1 : 2 : 3 : 5 : 6-pentamethylcoumaran, m.p. 119.5—120.5°, also obtained from $CHMe\text{-}CH\text{-}CH_2Cl$ and (I) at 150°; $CH_2\text{-}CH\text{-}CHEt\cdot OH$, first at 150° and then at 200°, gives 4-hydroxy-1 : 3 : 5 : 6-tetramethyl-2-ethylcoumaran, m.p. 88—89°. However, geraniol, first at 150° and then at 200°,

gives (?) impure 6-hydroxy-2 : 5 : 7 : 8-tetramethyl-2-isohexylechroman, b.p. 110—115° (liquid)/10⁻⁶ mm. (colour reactions of a 6-hydroxychroman). An oil, probably chiefly the trimethylallylcoumaran, is obtained from 2 : 6 : 1 : 4- $C_6H_3Me_3(OH)_2$ with $CH_2\text{-}CH\text{-}CH_2\text{-}OH$ and $ZnCl_2$ in C_6H_6 at 200° or $CH_2\text{-}CH\text{-}CH_2Br$ at 150°. Phytol, (I), and $ZnCl_2$ in boiling $AcOH\text{-}N_2$ give α -tocopherol (absorption spectrum). $CH_2(CH\text{-}CH_2)_2$, (I), $ZnCl_2$, and H_2SO_4 (1 drop) in boiling $AcOH$ give 6-hydroxy-5 : 7 : 8-trimethyl-2-ethylchroman, m.p. 115—116°. R. S. C.

Dibenzfuran. XIII. Orientation and substituted amines. H. GILMAN, P. T. PARKER, J. C. BAILIE, and G. E. BROWN (J. Amer. Chem. Soc., 1939, **61**, 2836—2845; cf. A., 1939, II, 440).—The rules of orientation previously postulated are borne out by the following reactions. 4-Bromo-1-methoxydibenzfuran (I) [prep. from 1-methoxydibenzfuran (II) by $Br\text{-}AcOH$], m.p. 97—97.5°, gives by Grignard reactions 1-methoxydibenzfuran-4-carboxylic acid (III), m.p. 279—280° (decomp.), and 1-methoxy-4- β -hydroxyethylidibenzfuran, m.p. 96—96.5°, b.p. 195—206°/2 mm., and thence (HBr) 1-methoxy-4- β -bromo-, m.p. 91—91.5°, and (NHEt₂) 1-methoxy-4- β -diethylaminoethylidibenzfuran [hydrochloride, m.p. 187° (decomp.)]. $AcCl\text{-}AlCl_3$ converts (II) in CS_2 into 4-acetyl-1-methoxydibenzfuran, m.p. 134—134.5° [oxidised by alkaline $KMnO_4$ to (III)], the oxime, m.p. 176—177.5°, of which with PCl_5 in C_6H_6 gives 4-acetamido-1-methoxy-, m.p. 222—223°, and thence 4-amino-1-methoxy-, m.p. 103—104°, 3-nitro-4-acetamido-1-methoxy-, m.p. 244°, and 3-nitro-4-amino-1-methoxydibenzfuran (IV), m.p. 206—207°. Addition of (IV) in C_5H_5N to $NaNO_2$ in $H_2SO_4\text{-}H_2O$ (2 : 1) at 5—10°, followed by $CO(NH_2)_2$ and heating with EtOH, gives 35% of 3-nitro-1-methoxydibenzfuran, m.p. 185—186°, hydrogenated (Raney Ni; EtOH; room temp./4 atm.) to 3-amino-1-methoxydibenzfuran, m.p. 127—127.5°. 2-Aminodibenzfuran (V) and $NH_2\text{-}CO\text{-}NH\text{-}NH_2$ in EtOH at room temp. give 2-dibenzfurylcarbamide, m.p. >325° (softens at 215—220°; tube), melts and resolidifies at 222—223° (block). Li 1-dibenzfuryl (prep. by $LiBu^a$) and $N_2\text{-}Br$ vapour give 40.5% of 1-bromodibenzfuran, m.p. 70—71°, converted by fuming HNO_3 into its 7- NO_2 -derivative (VI), m.p. 205°. Fuming HNO_3 converts 1-iododibenzfuran in AcOH into its 7- NO_2 -derivative, m.p. 224°, reduced by $H_2\text{-}Pd$ in abs. EtOH at 15 lb. to 2-nitrodibenzfuran (32%); when similarly reduced, (VI) gives (V). Me dibenzfuran-1-carboxylate, $AcCl$, and $AlCl_3$ in boiling CS_2 give Me 6-acetyldibenzfuran-1-carboxylate, m.p. 174—175°, the derived acid, m.p. 262—265°, from which with Cu-bronze in quinoline at 235—240° gives 3-acetyldibenzfuran. 2-Nitrodibenzfuran, $AcCl$, and $AlCl_3$ in $PhNO_2$ (not CS_2) give 2-nitro-6-acetyldibenzfuran, m.p. 212—213°, hydrogenated (Raney Ni; abs. EtOH; 100°/45 lb.) to 2-amino-6-acetyldibenzfuran, m.p. 158—159° [Ac derivative (prep. by Ac_2O in $AcOH\text{-}H_2O$), m.p. 203° (oxime, m.p. 203°), converted (diazo-reaction) into 3-acetyldibenzfuran], and oxidised by $CrO_3\text{-}AcOH$ [not $KMnO_4$], Br , $Na_2Cr_2O_7\text{-}H_2SO_4$, or $Ca(OCl)_2$ to 7-nitrodibenzfuran-3-carboxylic acid, decomp. 300° after softening at 295°. Dibenzfuran-2-carboxylic

acid (prep. by a Grignard reaction from the 2-Br-compound) and MeOH-HCl give the Me ester, converted by HNO₃ (conc. + fuming) into *Me 6-nitrodibenzfuran-2-carboxylate* (34.8%), m.p. 235–236° (corresponding acid, m.p. >330°, decarboxylated by Cu in hot quinoline to 3-nitrodibenzfuran), and some (?) 3-NO₂-ester, m.p. 202–203°. Addition of Br-AcOH to 2-aminodibenzfuran and NH₄CNS in 95% AcOH at 1–3° gives 2-amino-3-thiocyanodibenzfuran, m.p. 175° (resolidifies), converted by HCl in hot EtOH into 2-aminodibenzthiazolo-2':3'-4:5-thiazole (2-aminobenzfur[2:3-f]benzthiazole), m.p. 268–269° (hydrochloride, decomp. >300°). Dibenzfuran, AcCl, and AlCl₃ in CS₂ (less well, PhNO₂) give 46–57% of the 3-Ac derivative (VII) (oxime, m.p. 139–140°; NO₂-derivative, m.p. 290°), and 8% of the 3:6-Ac₂ derivative (VIII) [obtained rather better by Ac₂O or, best (32%), from (VII) by AcCl-AlCl₃-CS₂], m.p. 160° (lit. 140°). Oxidation of (VIII) gives dibenzfuran-3:6-dicarboxylic acid, obtained in poor yield from the 3:6-Br₂-compound (IX) by Mg, followed by CO₂, or better, by LiBu⁺, followed by CO₂ (CaPhI-CO₂ leads to 3:6-dibromodibenzfuran-1:8-dicarboxylic acid). Ca(OCl)₂ oxidises (VII) to the 3-carboxylic acid, m.p. 247–248°. AcCl-AlCl₃ converts (IX) in CS₂ into 3:6-dibromo-2-acetyldibenzfuran, m.p. 157–157.5°, the structure of which is proved by removing the Br by H₂-Pd-CaCO₃ and then oxidising by alkaline KMnO₄ to dibenzfuran-2-carboxylic acid. *Me* dibenzfuran-3-carboxylate (prep. from the acid by HCl-MeOH), m.p. 73–74°, gives a 7-NO₂-derivative, m.p. 239–240°. AcCl-AlCl₃-CS₂ converts 3-bromodibenzfuran into 3-bromo-6-acetyldibenzfuran, b.p. 205°/4 mm., oxidised by Ca(OCl)₂ to 6-bromodibenzfuran-3-carboxylic acid (X), m.p. 328°, debrominated by H₂-Pd-CaCO₃ to dibenzfuran-3-carboxylic acid. *Et* dibenzfuran-3-carboxylate (prep. from the acid by SOCl₂, followed by abs. EtOH), m.p. 54°, and Br-AcOH give mainly (28%) the 6-Br-ester, m.p. 130°, and thence by conc. HCl-AcOH (X). HNO₃ (*d* 1.5) and (I) in AcOH at 90–95° give 4-bromo-2-nitro-1-methoxydibenzfuran, m.p. 160–161°, hydrogenated (Pd-CaCO₃) to 2-amino-1-methoxydibenzfuran and reduced by SnCl₂-HCl to 4-bromo-2-amino-1-methoxydibenzfuran, m.p. 135–136° (Ac derivative, m.p. 178–179°). γ -Keto- γ -3-dibenzfuryl-*n*-butyric acid [prep. from dibenzfuran by (CH₃CO)₂O and AlCl₃ in PhNO₂-C₆H₅Cl₄ at 0–5°] is reduced (Zn-Hg-HCl-H₂O-PhMe) to γ -3-dibenzfuryl-*n*-butyric acid, cyclised by 88% H₂SO₄ to 1'-keto-1':2':3':4'-tetrahydronaphtha-7':6'-1:2-benzfuran (7-keto-7:8:9:10-tetrahydronaphtho[*b*]naphtho[2:3-*d*]furan) (XI), m.p. 137°, the oxime, m.p. 212–213°, of which is reduced by 2% Na-Hg in abs. EtOH (kept acid by AcOH) at 55–60° to the 1'-NH₂-compound (hydrochloride, m.p. 266–267°). NHMe₂·HCl, (CH₃O)₃, and (XI) in boiling C₅H₁₁OH give 2'-dimethylaminomethyl-1'-keto-1':2':3':4'-tetrahydronaphtha-7'-6'-1:2-benzfuran hydrochloride (14.3%), m.p. 185–186°. 3-Acetyldibenzfuran (XII) and HCO₂NH₄ in AcOH (etc.) give 2- α -aminoethylidibenzfuran hydrochloride, m.p. 222–223°. 3- α -Hydroxyethylidibenzfuran (prep. from Mg 3-dibenzfuryl bromide and MeCHO) and dry HBr give the bromide and thence (NH₄Et₂) 3- α -diethylaminodibenzfuran hydrobromide,

hygroscopic, and *picrate*, m.p. 173–174°. NHMe₂·HCl and (CH₃O)₃ in boiling, abs. EtOH convert (XII) into 3- β -dimethylaminopropionylidibenzfuran, m.p. 88–89° (hydrochloride, m.p. 194–195°). 2-Aminodibenzfuran (XIII) and *p*-C₆H₄Me·SO₃Et at 175–185° afford 2-ethylaminodibenzfuran (XIV), m.p. 69–70° [hydrochloride, m.p. 228–229°; NO-derivative, m.p. 136–137°, reduced by SnCl₂-HCl to (XIV)]. The Ac derivative of (XIII) and HNO₃ (*d* 1.5) in AcOH at 85–90° give 3-nitro-2-acetamidodibenzfuran, m.p. 196°, which with SnCl₂-HCl in AcOH yields 2-methylidibenzfuro-2':3'-4:5-glyoxaline, new m.p. 270° (hydrochloride, new m.p. >335°). 3-Nitro-4-acetamido-1-methoxydibenzfuran gives similarly 1'-methoxy-2-methylidibenzfuro-3':4'-4:5-glyoxaline, m.p. 222–222.5° [hydrochloride, m.p. 306–307° (decomp.)]. 7-Acetamido-3-acetyldibenzfuran and HNO₃ (*d* 1.5) in AcOH at 100° give the 6-NO₂-derivative, m.p. 270–271°, and thence by H₂-Raney Ni in EtOH at 100°/45 lb. 7'-acetyl-2-methylidibenzfuro-2':3'-4:5-glyoxaline, m.p. 298° [hydrochloride, m.p. ~325° (decomp.)]. Li 1-dibenzfuryl and isoquinoline in Et₂O at 0–5° give 1-1'-dibenzfurylisoquinoline (11.3%), m.p. 137–138° (hydrochloride, hydrolysed in H₂O). Dibenzfuran-1-carboxylic acid (XV) and SOCl₂ give the chloride, which with CH₃N₂ in Et₂O yields 1-dibenzfuryl CHN₂ ketone, m.p. 72–75°. When this is treated in dioxan at 100° with conc., aq. NH₃ and then with AgNO₃, it yields 1-dibenzfurylacetylamide, m.p. 211–212°, hydrolysed to 1-dibenzfurylacetic acid, m.p. 213.5–214.5°, the acid chloride of which in Et₂O with 3:4:1-(OMe)₂C₆H₃·CO·CH₂NH₂ gives α -1'-dibenzfurylacetylamido-3:4-dimethoxyacetophenone, m.p. 186–187°. The acid chloride of (XV) similarly gives α -dibenzfuryl-1'-carboxylamido-3:4-dimethoxyacetophenone, m.p. 178–179°. R. S. C.

Dibenzfuran. XIV. Diazo-coupling 1-, 2-, and 3-hydroxy-compounds. H. GILMAN and M. W. VAN ESS. XV. 1:4- and 1:4:8-Derivatives. H. GILMAN and L. C. CHENEY (J. Amer. Chem. Soc., 1939, **61**, 3146–3148, 3149–3156).—XIV. 3-, 2-, and 1-Hydroxydibenzfuran and PhN₂Cl in aq. KOH give 3-hydroxy-4-, m.p. 165.5–166°, 2-hydroxy-3-, m.p. 177–178°, and 1-hydroxy-4-benzene-azodibenzfuran, m.p. 174–175°, respectively, which indicates lability of the ethylenic linkings. Structures are proved by reduction (SnCl₂-HCl-AcOH) to the unstable aminohydroxydibenzfurans and conversion of the hydrobromides thereof by aq. NaNO₂-CuSO₄, followed by CuBr-HBr, into the known bromohydroxydibenzfurans.

XV. 1-Hydroxy-8-methoxydibenzfuran (I) with HBr (*d* 1.49) in AcOH gives 1:8-dihydroxydibenzfuran (II), new m.p. 200–202° (Ac₂ derivative, m.p. 177°), and with Me₂SO₄-60% KOH gives 1:8-dimethoxydibenzfuran (III), m.p. 128–129° (*picrate*, m.p. 161–162°), which with AcCl-AlCl₃ in PhNO₂ gives 60% of 4-acetyl-1:8-dimethoxydibenzfuran, m.p. 178.5–179.5°. The oxime, m.p. 203–204°, thereof is converted by PCl₅ in C₆H₆ into 4-acetamido-, m.p. 244–245°, and thence (HCl-EtOH) into 4-amino-1:8-dimethoxydibenzfuran (IV), m.p. 162–162.5°. PhN₂Cl couples with (I) in dil., aq. KOH to give 1-hydroxy-4-benzeneazo-8-methoxydibenzfuran, m.p. 175°,

converted by $\text{Me}_2\text{SO}_4\text{--KOH--COMe}_2$ into 4-benzeneazo-1:8-dimethoxydibenzfuran, m.p. 170°, and thence ($\text{SnCl}_2\text{--HCl--AcOH}$) into (IV). Addition of AlCl_3 (1.1 mol.) to 1-methoxydibenzfuran (V) (1 mol.) and COCl_2 (0.55 mol.) in PhNO_2 gives di-1-methoxy-4-dibenzfuryl diketone (34.6%), m.p. 239°, and ketone (18%), m.p. 234°, with some 1-methoxydibenzfuran-4-carboxylic acid (VI), m.p. 276—277°. With $\text{CH}_2\text{Cl}\cdot\text{COCl}$ and AlCl_3 in PhNO_2 , (V) gives 4-chloroacetyl-1-methoxydibenzfuran, m.p. 165—166°, and with $\text{CO}_2\text{Et}\cdot\text{COCl--AlCl}_3$ in PhNO_2 gives Et 1-methoxydibenzfuran-4-glyoxylate, m.p. 113°, hydrolysed to the acid, m.p. 187° [semicarbazone, m.p. 211.5—212° (decomp.)], which with alkaline KMnO_4 gives (VI). (COCl)₂, AlCl_3 , and (III) in PhNO_2 give di-1:8-dimethoxydibenzfuryl diketone (60.7%), m.p. >300°, and ketone (10.4%), m.p. 254—255°, with some 1:8-dimethoxydibenzfuran-4-carboxylic acid (VII), m.p. 297—298° (Me ester, m.p. 163°). 2-Hydroxy-1-methoxydibenzfuran (VIII) yields (HBr--AcOH) 1:2-dihydroxydibenzfuran, m.p. 164—164.5° (Ac_2 derivative, m.p. 104—105°), and ($\text{Me}_2\text{SO}_4\text{--10% NaOH}$) 1:2-dimethoxydibenzfuran (IX), m.p. 60—61°. AcCl--AlCl_3 in PhNO_2 converts (IX) into 4-acetyl-1:2-dimethoxydibenzfuran, m.p. 90.5—91° (some demethylation occurs), the oxime, m.p. 156—157°, of which with PCl_5 in C_6H_6 gives 4-acetamido-, m.p. 196—196.5°, and thence (KOH--EtOH) 4-amino-1:2-dimethoxydibenzfuran (X), m.p. 162.5—163°. 4-Bromo-1:2-dimethoxydibenzfuran (XI) [prep. from (IX) by Br--AcOH], m.p. 108°, with CuBr--aq. NH_3 at 220—230° gives (X). With Br in AcOH , (III) gives 4-bromo-, m.p. 152°, or 4:5-dibromo-1:8-dimethoxydibenzfuran (XII), m.p. 167—168°, and (II) gives 4:5-dibromo-1:8-dihydroxydibenzfuran, m.p. 239—240° [converted into (XII) by Me_2SO_4], but (I) gives (? 2:4-)dibromo-1-hydroxy-8-methoxy-, m.p. 177—178°, and thence (? 2:4-)dibromo-1:8-dimethoxydibenzfuran, m.p. 173.5—174°. Br--AcOH converts (VIII) into 4-bromo-2-hydroxy-1-methoxydibenzfuran (54.6%), m.p. 161—162° (and an isomeride), also obtained ($\text{NaNO}_2\text{--H}_2\text{SO}_4$; CuSO_4) from 4-bromo-2-amino-1-methoxydibenzfuran and converted by $\text{Me}_2\text{SO}_4\text{--10% NaOH}$ into (XI). 1-Bromo-8-methoxydibenzfuran with HI (d 1.67) gives 19% of 1-bromo-8-hydroxydibenzfuran, m.p. 138—139°, and with CuBr--aq. NH_3 , first at 100° and then at 215°, gives 1-amino-8-methoxydibenzfuran (51%), m.p. 109° [hydrochloride, m.p. 235—236° (decomp.)], and thence (HBr--AcOH) 1-amino-8-hydroxydibenzfuran, m.p. 191.5—192.5° [hydrochloride, m.p. 265—266° (decomp.)]. NaHSO_3 , aq. NH_3 , and (II) at 185—195° give 1:8-diaminodibenzfuran, m.p. 152° [dihydrochloride, m.p. 297—298° (decomp.)]; picrate, m.p. 213° (decomp.); Ac_2 derivative, m.p. 297—298° (lit. 322.5—323.5°). PhN_2Cl and (II) in aq. KOH give the impure 2:4:5-(PhN_2)₃-derivative, m.p. 228° (decomp.), methylated in COMe_2 to 2:4:5-tribenzeneazo-1:8-dimethoxydibenzfuran, m.p. 190—191°. (VII) is obtained from the 4-Ac compound by $\text{I--KI--NaOH--dioxan}$ and from the 4-Br compound by the Grignard reaction; with SOCl_2 it gives the acid chloride, m.p. 147—150°, which with $\text{NO}\cdot\text{NMe}\cdot\text{CO}_2\text{Et}$ in dioxan gives 1:8-dimethoxy-4-dibenzfuryl $\text{C}_6\text{H}_5\text{N}_2$ ketone, m.p. 151° (gas), converted by $\text{AgNO}_3\text{--NH}_3\cdot\text{H}_2\text{O--dioxan}$ at 100° into 1:8-

dimethoxy-1-dibenzfurylacetamide, m.p. 210—211°, and thence by $\text{NaOH--H}_2\text{O--EtOH}$ into 1:8-dimethoxy-1-dibenzfurylacetic acid, m.p. 205.5—206.5°. Diazotisation and SnCl_4 -reduction of the 2- NH_2 -compound affords 2-hydrazinodibenzfuran, m.p. 174—175° (lit. 152°) [hydrochloride, m.p. 242—243° (decomp.) (lit. 225°)]. Na--EtOH reduces 1-aminodibenzfuran in N_2 to 1-amino-5:6:7:8-tetrahydrodibenzfuran, an oil [hydrochloride, m.p. 228° (decomp.; darkens at 214°)], which gives no carbonate and by diazotisation and coupling with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ gives a red dye, m.p. 199—201°.

R. S. C.

Chromones of the naphthalene series. I. Transformation of o-aroxyoxyacetoarones into o-hydroxydiarylmethanes. II. Synthesis of linear naphthaflavone (6:7-benzoflavone). V. V. VIRKAR and T. S. WHEELER (J.C.S., 1939, 1679—1681, 1681—1683).—I. Na causes the rearrangement of o-aroxyoxyacetoarones into the corresponding o-hydroxydiarylmethanes, which can be cyclised to the chromones. The following are described: 1-1', m.p. 135°, and 1-2'-naphthoiloxy-, m.p. 113—114°, and 1-3'-methoxy-2'-naphthoiloxy-2-acetonaphthone, m.p. 119°; 1-hydroxy-2:1'-dinaphthoilmethane, m.p. 142°, cyclised to 2-1'-naphthyl-7:8-benzochromone, m.p. 205°; 1-hydroxydi-2-naphthoilmethane, m.p. 164°, cyclised (HBr) to 2-2'-naphthyl-7:8-benzochromone, m.p. 190—191°; 1-hydroxy-3'-methoxy-2:2'-dinaphthoilmethane, m.p. 163°, cyclised to 2-(3'-methoxy-2'-naphthyl)-, m.p. 204—205°, and 2-(3'-hydroxy-2'-naphthyl)-7:8-benzochromone, m.p. >300° (Ac derivative, m.p. 180—181°). A similar method is applied to the synthesis of some 2-naphthylbenzochromones.

II. Benzoyl-2-methoxy-3-naphthoilmethane, m.p. 98°, is prepared from Na, COPhMe , and 2:3- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Me}$; o-anisoyl-2-methoxy-3- (I), m.p. 120—122°, and 3-methoxydi-2-naphthoilmethane, m.p. 160°, di-(1-methoxy-2-naphthoilmethane), m.p. 122°, and 2:2'-dimethoxy-1:2'-dinaphthoilmethane, m.p. 163°, are similarly obtained. Bromo-o-anisoyl-2-methoxy-3-naphthoilmethane, m.p. 152°, is formed by bromination of (I). Cyclisation can be effected with HBr--AcOH or $\text{HI--Ac}_2\text{O}$: 6:7-benzoflavone, m.p. 171—172°; 2'-methoxy-, m.p. 165°, -hydroxy-, m.p. 256—257°, and -acetoxy-6:7-benzoflavone, m.p. 136—138°. These compounds with NaOEt give 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{COMe}$ and 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$. The following are similarly prepared: 2-2'-naphthyl-6:7-, m.p. 193°, 2-(1'-methoxy-, m.p. 151—152°, 2-(1'-hydroxy-, m.p. >280°, and 2-(1'-acetoxy-2'-naphthyl)-7:8-, m.p. 174°, and 2-(2'-methoxy-, m.p. 197°, 2-(2'-hydroxy-, m.p. 283—285°, and 2-(2'-acetoxy-1'-naphthyl)-6:7-benzochromone, m.p. 148—150° [the latter compounds may be 2-(3'-methoxy-2'-naphthyl)-5:6-benzochromones].

F. R. S.

Monoalkyldioxans. R. K. SUMMERBELL and R. R. UMHOEFFER (J. Amer. Chem. Soc., 1939, 61, 3016—3019).—Adding freshly prepared chlorodioxan (I) to MgRX (excess; whether or not treated with ZnCl_2 or CdCl_2) in Et_2O gives 2-methyl-, b.p. 109—110°/746.5 mm., 2-ethyl- (II), b.p. 132.5—133°/750 mm., 2-n-propyl-, b.p. 155.6—157.1° (corr.)/746 mm., 2-n-butyl-, b.p. 178—179° (corr.)/735 mm., and 2-allyl-dioxan (III), b.p. 156—158°/747.6 mm. If the (I)

contains dioxen, $\text{MgBu}^{\text{c}}\text{Br}$ (ZnCl_2 present) or MgEtBr gives also some 2-dioxanyl-3-n-butyl-, m.p. 101–102°, or 3-ethyl-dioxan, m.p. 97.5°, respectively. $(\text{CH}_2\cdot\text{OH})_2$ is formed by boiling (III) with Na, but other analogous compounds are stable. The solubility in H_2O decreases and the unpleasantness of the odour increases with increase in mol. wt. of the alkyl. The alkylidioxans do not add picric acid or quinol.

$\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CHMeCl}$ (prep. from paraldehyde, $\text{Cl}\cdot[\text{CH}_2]_2\cdot\text{OH}$, and HCl at 0°) and Br at 0° give β -chloroethyl α -dibromoethyl ether, b.p. 108°/12 mm., converted by MgEtBr into β -chloroethyl α -bromo-methyl-n-propyl ether, b.p. 92–93°/12 mm., which with 10% KOH at 200–205° gives 17% of (II). 2:3-Dichlorodioxan (2 mols.), Mg (3.4 atoms), and I (0.4 atom) in Et_2O give 49% of dioxen, b.p. 93–95°.

R. S. C.

Dioxadiene. R. K. SUMMERBELL and R. R. UMHOEFER (J. Amer. Chem. Soc., 1939, 61, 3020–3022).—2:3:5:6-Tetrachlorodioxan (I), Mg , and MgI_2 in boiling $\text{Bu}^{\text{a}}_2\text{O}$ (not Et_2O) give dioxadiene, b.p. 75°/746 mm., insol. in H_2O , which with $\text{Br}\cdot\text{CCl}_4$ at 0° gives the 2:3-dibromide (no HBr liberated), m.p. 58°, with Cl_2 gives (I), with $\text{HCl}\cdot\text{CCl}_4$ gives 2:5-dichlorodioxan (also obtained by chlorinating dioxan), m.p. 118–119°, and polymerises to a solid, m.p. >250°, when kept. Other methods of prep. failed.

R. S. C.

Reaction of a thiophen derivative with maleic anhydride. D. B. CLAPP (J. Amer. Chem. Soc., 1939, 61, 2733–2735).—2:3:4:5-Di-1':8'-naphthyl-enethiophen (I), m.p. 285.5–286° (corr.), and $(\text{CH}\cdot\text{CO})_2\text{O}$ at 225° give an adduct, which spontaneously loses H_2S and yields 3:4:5:6-di-1':8'-naphthyl-enephthalic anhydride, decomp. ~385°. Stilbene and (I) at 310–320° similarly give H_2S and 1:2-diphenyl-3:4:5:6-di-1':8'-naphthylenebenzene, m.p. 290–291° (corr.). Cl_2 and Br give dissociable adducts with (I).

R. S. C.

β -Phenylfurylethylamine and analogous derivatives of thiophen and pyrrole. (SIR) R. ROBINSON and W. M. TODD (J.C.S., 1939, 1743–1747).—*Et* β -2-(5-phenylpyrryl)propionate, m.p. 103°, with N_2H_4 gives β -2-(5-phenylpyrryl)-propionhydrazide, m.p. 137°, which with NaNO_2 affords the ethylamine hydrochloride, m.p. 225°. 4:7-Diketo-7-phenylhept-oic acid (*Et* ester, m.p. 23–25°), P_2O_5 , and C_6H_6 yield β -2-(5-phenylfuryl)-propionic acid, m.p. 116°, the *Et* ester, b.p. 165–167°/2–3 mm., m.p. 20–21°, of which with N_2H_4 affords the propionhydrazide, m.p. 110°, converted through *Me* β -2-(5-phenylfuryl)ethyl-carbamate, m.p. 59–60°, into β -2-(5-phenylfuryl)-ethylamine hydrochloride, m.p. 205–206° (picrate, m.p. 200°; *Bz*, m.p. 121°, and *Ac* derivatives, m.p. 72°). A similar series of reactions with *Me* 4:7-diketo-7-phenylheptate, b.p. 197°/2 mm., m.p. 41°, and P_2S_5 gives *Me* β -2-(5-phenylthienyl)propionate (+0.5 H_2O), m.p. 75° [acid (+0.5 H_2O), m.p. 148°], β -2-(5-phenylthienyl)propionhydrazide, m.p. 151°, *Me* β -2-(5-phenylthienyl)-ethylcarbamate, m.p. 100°, and the ethylamine hydrochloride, m.p. 266° (picrate, m.p. 217°; *Bz*, m.p. 141°, and *Ac* derivatives, m.p. 128°). Furfurylidene-p-methoxyacetophenone, m.p. 79°, with $\text{HCl}\cdot\text{EtOH}$ affords 4:7-diketo-7-p-methoxyphenyl-hept-oic acid, m.p. 119°, and this yields β -2-(5-p-

methoxyphenylpyrryl)-propionic acid, m.p. 170–171° (*Et* ester, m.p. 103°), and propionhydrazide, m.p. 169°, which could not be converted into the amine. β -2-(5-p-Methoxyphenylfuryl)propionic acid, m.p. 141° (*Et* ester, b.p. 189–195°/2 mm., m.p. 52°), gives the hydrazide, m.p. 136°, ethylamine hydrochloride, m.p. 240°, and *Me* β -2-(5-p-methoxyphenylfuryl)ethylcarbamate, m.p. 89°. *Me* 4:7-diketo-7-p-methoxyphenyl-heptate, b.p. 248°/3 mm., m.p. 48°, forms with P_2S_5 β -2-(5-p-methoxyphenylthienyl)propionic acid, m.p. 178° (*Me* ester, m.p. 94°), hydrazide, m.p. 112°, ethylamine hydrochloride, m.p. 283° (*Ac* derivative, m.p. 145°), and *Me* β -2-(5-p-methoxyphenylthienyl)ethylcarbamate, m.p. 112°. 4:7-Diketo-oct-oic acid and P_2O_5 yield β -2-(5-methylfuryl)propionic acid, m.p. 54–55°, which with $\text{EtOH}\cdot\text{H}_2\text{SO}_4$ gives a mixed product, containing *Et* β -2-(5-methylfuryl)propionate, b.p. 97°/2–3 mm. With CH_2N_2 *Me* β -2-(5-methylfuryl)propionate, b.p. 83°/2–3 mm., and *Me* 4:7-diketo-octate, b.p. 140°/4 mm., are obtained. β -2-(5-Phenyltetrahydrofuryl)ethylamine hydrochloride, m.p. 122°, is prepared by reduction ($\text{Pd}\cdot\text{C}\cdot\text{H}_2$) of the corresponding phenylfuryl compound. F. R. S.

Action of p-tolylthiocarbimide on ethyl acet-onedicarboxylate. D. E. WORRALL (J. Amer. Chem. Soc., 1939, 61, 2966–2969).—Addition of powdered Na (1 atom) in Et_2O , followed by *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NSC}$ (1 mol.), to $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (I) gives *Et* 2:4-diketo-6-thio-1-p-tolylpiperidine-5-carboxylate (II), m.p. 174–175° (decomp.), sol. in Na_2CO_3 and pptd. therefrom by HCl but not by AcOH (blue-green ppt. with FeCl_3). AcOH only slowly decomposes (II), more rapidly if $\text{NHPh}\cdot\text{NH}_2$ is added. Hot $\text{KOH}\cdot\text{EtOH}$ hydrolyses and decarboxylates (II), yielding 2:4-diketo-6-thio-1-p-tolylpiperidine, m.p. 158–159° (decomp.). MeI and (II) in warm EtOH give *Et* 2:4-diketo-6-methylthiol-1-p-tolyl-1:2:3:4-tetrahydropyridine-5-carboxylate (III), m.p. indefinite, >250° (decomp.) (*Na* salt), stable to AcOH or $\text{AcOH}\cdot\text{NHPh}\cdot\text{NH}_2$. $\text{Br}\cdot\text{AcOH}$ and (II) at 100° give the 3-*Br*-derivative, m.p. 238–239°, also sol. in Na_2CO_3 . (II) similarly gives its 3-*Br*-derivative, m.p. 165.5–166.5°. With $\text{Me}_2\text{SO}_4\cdot\text{NaOH}$, (II) gives *Et* 6-methylthiol-4-methoxy-1-p-tolyl-2-pyridone-5-carboxylate, m.p. 166°, insol. in NaOH and stable to Br . With 2 Na and 2 mols. of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NSC}$, (I) gives *Et* 2:4-diketo-6-thio-1-p-tolylpiperidine-3-thioform-p-toluidide-5-carboxylate (IV), m.p. 182–184° (decomp.), sol. in alkali, fairly stable to AcOH , converted by MeI in boiling EtOH into *Et* 2:4-diketo-6-methylthiol-1-p-tolyl-1:2:3:4-tetrahydropyridine-3-thioform-p-toluidide-5-carboxylate (V), m.p. 151–152°, sol. in Na_2CO_3 , stable to AcOH , and converted by boiling $\text{KOH}\cdot\text{EtOH}$ into the corresponding 5-carboxylic acid, m.p. 232–233° (decomp.). Boiling $\text{KOH}\cdot\text{EtOH}$ converts (IV) into 2:4-diketo-6-methylthiol-1-p-tolyl-1:2:3:4-tetrahydropyridine-5-thioform-p-toluidide, m.p. 205–208°, sol. in Na_2CO_3 , reactive to Br . The *Na* derivative of (V) with MeI in aq. EtOH at 100° (tube) gives 6-methylthiol-4-methoxy-1-p-tolyl-2-pyridone-3-thioform-p-toluidide, m.p. 153°, insol. in alkali, stable to Br . $\text{Me}_2\text{SO}_4\cdot\text{NaOH}$ converts (IV) into *Me* 6-methylthiol-4-methoxy-1-p-tolyl-2-pyridone-3:5-dicarboxylate, m.p. 177–178°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$. Br and (IV)

in AcOH at 100° give HBr and *Et* 2 : 4-diketo-6-thio-1-*p*-tolyl-3-5'-methyl-1'-benzthiazolylpiperidine-5-carboxylate, m.p. >300° (evolves H₂S readily with NHPH·NH₂·AcOH), sol. in alkali, hydrolysed rapidly by cold, aq. NH₃ to the 5-carboxylic acid, m.p. 260—261° (decomp.; gas), and converted by Mel-EtOH-NH₃ into *Et* 2 : 4-diketo-6-methylthiol-1-*p*-tolyl-3-5'-methyl-1'-benzthiazolyl-1 : 2 : 3 : 4-tetrahydropyridine-5-carboxylate, m.p. 282—283° (decomp.), stable to Br or NHPH·NH₂ but hydrolysed by aq. NH₃. R. S. C.

β-Arylaminoacrylic esters. II. Use of β-arylaminoacrylic esters for synthesis of N-aryl substituted pyridonecarboxylic acids. M. V. RUBTZOVA (J. Gen. Chem. Russ., 1939, 9, 1517—1524).—The reaction $2\text{NHR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \rightarrow$

$\text{NR}(\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et})_2 \rightarrow \text{NR} \begin{array}{c} \text{CH}\cdot\text{C}(\text{CO}_2\text{H}) \\ \text{CH}=\text{CH} \end{array} \text{CO}$ is of

general application. β-C₁₀H₇·NH₂ in AcOH and OH·CH·CH·CO₂Et give *Et* β-(2-naphthylamino)acrylate, m.p. 134·5—135°, which, heated in vac. at 125—130° for 9 hr., and then hydrolysed (MeOH-KOH), yields two forms (probably *syn*- and *anti*-) of 1-β-naphthyl-4-pyridone-3-carboxylic acid, m.p. 306—307° and 252—253° (decomp.). The following are prepared analogously: *Et* β-anilino-, m.p. 105—106°, and *Et* β-(6-quinolylamino)-acrylate, m.p. 155—156°, *Et* β-(6-quinolylamino)diacrylate, m.p. 127—128°, 1-phenyl-, m.p. 265—266° (chloride, m.p. 107—108°), and 1-(6'-quinolyl)-4-pyridone-3-carboxylic acid, m.p. 353—355° (decomp.) (chloride, m.p. 262—263°; *Et* ester, m.p. 116—117°; diethylamide, m.p. 155—156°). R. T.

Synthesis in the 1 : 2 : 3 : 4-tetrahydroquinoline series. W. S. EMERSON and J. W. DAVIS (J. Amer. Chem. Soc., 1939, 61, 2830—2832).—2 : 8-[zincichloride, m.p. 270° (decomp.)] and 2 : 6-dimethylquinoline (picrate, new m.p. 186—187°; zincichloride, m.p. 211·5—213°; methiodide, new m.p. 239—240°) are reduced by Sn-HCl to 2 : 8- (I), b.p. 250—255° [picrate, m.p. 159·5—160°; zincichloride, m.p. 270° (decomp.); *Bz* derivative, m.p. 118·5—120°], and 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (II), b.p. 147—149°/24 mm. (*Bz* derivative, m.p. 104—105°; picrate, m.p. 165—169°, unstable; zincichloride, m.p. 187—195°). With Mel at room temp. (I) gives 1 : 2 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b.p. 130°/21 mm. (hydriodide, m.p. 154·5—155·5°; picrate, m.p. 177—178°; zincichloride, m.p. 213—214°; hydriodide, m.p. 155—157°). Mel reacts more violently with (II), yielding the 1 : 2 : 6-Me₃ compound, b.p. 145°/20 mm. (hydriodide, m.p. 187·5—188·5°; picrate, m.p. 141—142°). R. S. C.

Use of alkoxy-ketones in the synthesis of quinolines by the Pfitzinger reaction. L. B. CROSS [with H. R. HENZE] (J. Amer. Chem. Soc., 1939, 61, 2730—2733).—COMe·CH₂·OEt (prep. in 65% yield from OEt·CH₂·CN and MgMel), b.p. 34—36°/28 mm., isatin, and 33% KOH at 100° give 44% of 3-ethoxy-2-methylquinoline-4-carboxylic acid (I), m.p. 243° (decomp.), which at 250° gives CO₂ and 3-ethoxy-2-methylquinoline (II), m.p. 68—69°, b.p. 140—141°/2—3 mm. With conc. HCl at 150°, (I) gives 3-hydroxy-2-methylquinoline-4-carboxylic acid, m.p. 242—244° (decomp.), and (II) gives similarly 3-hydroxy-2-methylquinoline (III), darkens at ~250°,

m.p. 260° [picrate, m.p. 192—194° (lit. 191°)], also obtained from (II) by HI-red P at 150°. *o*-C₆H₄(CO)₂O at 200° converts (III) or (I) into the phthalone, m.p. 264—266°, of (III). COEt·CH₂·OEt, 5-methylisatin, and 33% KOH at 100° give 3-ethoxy-6-methyl-2-ethylcinchonine acid, m.p. 222° (decomp.). 3-Ethoxy-2-ethylcinchonine acid (IV), m.p. 199—201° (decomp.), 3-ethoxy-2-ethylquinoline (V), m.p. 58·5°, b.p. 138—140°/3—4 mm. (hydriodide, m.p. 190—197°), and 3-hydroxy-2-ethylquinoline (VI), m.p. 206—208° (decomp.), are also prepared. HI-red P at 125° converts (IV) into 3-hydroxy-2-ethylcinchonine acid, m.p. 208—209° (decomp.), but at 150° some (V) is also formed. Sn-HCl reduces (VI) to 2-ethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b.p. 125—127°/7 mm. (picrate, m.p. 143—145°). M.p. are corr. R. S. C.

Nitrogen compounds in petroleum distillates.

XV. Countercurrent acid extraction of kero bases. Isolation of 2 : 4-dimethyl-8-*n*-propylquinoline. W. N. AXE and J. R. BAILEY. **XVI. Use of multiple acid extraction in isolation of 2 : 3 : 4-trimethyl-8-ethylquinoline.** R. A. GLENN and J. R. BAILEY. **XVII. Use of multiple acid extraction in isolation of 2 : 3 : 4-trimethyl-8-*n*-propylquinoline.** L. M. SCHENCK and J. R. BAILEY (J. Amer. Chem. Soc., 1939, 61, 2609—2612, 2612—2613, 2613—2615; cf. A., 1939, II, 342).—XV. Countercurrent extraction (described) of aromatic petroleum bases (best previously fractionated by decomp. of the sulphites) (b.p. 292—293°) by HCl and subsequent purification by way of the picrates and zincichlorides yields 2 : 3-dimethyl-8-ethyl-, 2 : 3-dimethyl-8-*n*-propyl-, and 2 : 4-dimethyl-8-*n*-propylquinoline (I), b.p. 298°/747 mm. (zincichloride, m.p. 225—226°; phthalone, m.p. 198—199°). With K₂Cr₂O₇-H₂SO₄, (I) gives 2 : 4-dimethylquinoline-8-carboxylic acid, decarboxylated by soda-lime distillation to 2 : 4-dimethylquinoline. The structure of (I) is finally proved by synthesis from *o*-C₆H₄Pr^o·NH₂ and CH₂Ac·COMe. Countercurrent acid extraction of other fractions of bases is described.

XVI. Multiple acid extraction and subsequent countercurrent acid extraction of a basic fraction, b.p. 305—315°, yields 2 : 3 : 4-trimethyl-8-ethylquinoline, m.p. 52·5—53°, b.p. 320° [picrate, m.p. 216°; phthalone, m.p. 253°; nitrate, m.p. 159·5—160° (decomp.); *H* sulphate, m.p. 245—246°; hydrochloride, m.p. 203—204°], oxidised to 2 : 3 : 4-trimethylquinoline-8-carboxylic acid (II) and synthesised by condensing CHMeAc·COMe with *o*-C₆H₄Et·NH₂ and cyclising by H₂SO₄ the anil formed.

XVIII. Cumulative and countercurrent extraction of the aromatic bases, b.p. 320—330°, give 2 : 3 : 4-trimethyl-8-*n*-propylquinoline, m.p. 69—70°, b.p. 330° [nitrate, m.p. 160·1° (decomp.); picrate, m.p. 211—211·5°; *H* sulphate, m.p. 230·5—231°; hygroscopic hydrochloride, m.p. 221—222°], obtained also in smaller yield from transformer oil, oxidised to (II), and synthesised (two steps) in ~90% yield from *o*-C₆H₄Pr^o·NH₂ and CHMeAc·COMe. R. S. C.

Synthesis of substituted quinolines and 5 : 6-benzquinolines. R. G. GOULD, jun., and W. A. JACOBS (J. Amer. Chem. Soc., 1939, 61, 2890—2895).—2 : 4-NH₂·C₁₀H₆·CO₂H and CH₂Ac·CO₂Et in MeOH

at room temp. give *Et* β -4-carboxy-2-naphthylamino-crotonate, m.p. 157—158°, cyclised by addition to kerosene at 250—265° in N_2 to 4-hydroxy-2-methyl-5:6-benzquinoline-7-carboxylic acid (I), m.p. >360° [hydrochloride; *Me*, m.p. 295—296° (decomp.), and *Et* ester, m.p. 295—297°]. *Et* β -3-naphthostyryl-aminocrotonate [prep. from 3-aminonaphthostyryl (II) and $CH_3Ac \cdot CO_2Et$ in boiling EtOH], m.p. 180—182°, is similarly cyclised to 4-hydroxy-6-methylnaphthostyrylo-3':4'-2:3-pyridine, m.p. >360° (hydrochloride) $CHAc(CO_2Et)_2$ and NH_2Ph at room temp. give NH_2Ac and $NHPh \cdot CMe_2C(CO_2Et)_2$ (not purified), cyclised to *Et* 4-hydroxy-2-methylquinoline-3-carboxylate, m.p. 104—107° [corresponding acid, new m.p. 245—247° (decomp.)]. (II) and $CHAc(CO_2Et)_2$ give slowly 3- α -carbethoxyacetoacetamidonaphthostyryl, m.p. 268—270° (decomp.). Cyclisation of $NHPh \cdot CH_2C(CO_2Et)_2$ gives 4-hydroxyquinoline-3-carboxylic acid, new m.p. 267—268°. 1:4- $NH_2 \cdot C_{10}H_6 \cdot COMe$ and $OEt \cdot CH_2C(CO_2Et)_2$ (III) at 100° give *Et* 4-carbomethoxy-1-naphthylaminomethylenemalonate, m.p. 89—90°, cyclised to a *Me*₁ ester, hydrolysis of which gives 4-hydroxy-5:6-benzquinoline-3:7-dicarboxylic acid, m.p. 360°, reduced by Zn-Hg in AcOH to 4-keto-1:2:3:4-tetrahydronaphthostyrylo-3':4'-1:2-pyridine-5-carboxylic acid, m.p. >350°. Boiling (II) and (III) in EtOH gives *Et* 3-carbostyrylaminomethylenemalonate, m.p. 231—232°, cyclised to an ester, yielding by NaOH 4-hydroxycarbostyryl-3':4'-2:3-pyridine-5-carboxylic acid, m.p. >360°. CCl_4 , (I), a little Cu powder and EtOH in boiling 50% aq. KOH give 4-hydroxy-2-methyl-5:6-benzquinoline-3:7-carboxylic acid, m.p. >360° [*Me*₁ (prep. by $HCl \cdot MeOH$), m.p. 290—295° (decomp.) (hydrochloride), and *Me*₂ ester (prep. in poor yield by $MeOH \cdot H_2SO_4$), m.p. 239—240°; *Me* ether *Me*₂ ester (prep. by CH_2N_2), m.p. 142—144°], converted by HNO_3 (d 1.58) into mixed $(NO_2)_1$ -derivatives, which with $Fe(OH)_2$ give 4-hydroxy-2-methylnaphthostyrylo-4':3'-5:6-pyridine-3-carboxylic acid (IV), m.p. >360°, and α -amino-4-hydroxy-2-methyl-5:6-benzquinoline-3:7-dicarboxylic acid, m.p. >360°. 2:4- $NH_2 \cdot C_{10}H_6 \cdot CO_2Me$, $AcCO_2H$, and $MeCHO$ in boiling EtOH give 7-carbomethoxy-2-methyl-5:6-benzquinoline-4-carboxylic acid, m.p. 265—266° (decomp.), hydrolysed to the 4:7-dicarboxylic acid, m.p. 298—299° (decomp.), and oxidised by SeO_2 in C_6H_5N to 7-carbomethoxy-5:6-benzquinoline-2:4-dicarboxylic acid, $+C_6H_5N$, m.p. 199—200° (decomp.) [yields 5:6-benzquinoline-2:4:7-tricarboxylic acid, m.p. 285—286° (decomp.)]. Similarly (II) gives 2-methylnaphthostyrylo-4':3'-5:6-pyridine-4-carboxylic acid, m.p. 240—242° (decomp.). $\beta \cdot C_{10}H_7 \cdot NH_2$ and epichlorohydrin give 3-hydroxy-1:2:3:4-tetrahydro-5:6-benzquinoline, m.p. 82—83° (hydrochloride).

R. S. C.

isoQuinoline derivatives.—See B., 1939, 1295.

Acridine derivatives.—See B., 1939, 1295.

Phenanthridine derivatives.—See B., 1939, 1216.

Benzanthrones.—See B., 1939, 1215.

Substituted dialuric and hydurilic acids.

C. M. MARBERG and D. W. STANGER (J. Amer. Chem. Soc., 1939, 61, 2736—2737).—5-isoAmylbarbituric acid and H_2O_2 give 5-isoamylidialuric acid, $+2H_2O$,m.p. 179.5—180° (5-Bz derivative, m.p. 210.5—216°; hydrolysed by NaOH to isoamyltartronic acid), also obtained with some 5:5'-diisoamylhydruilic acid, $+2H_2O$, m.p. 290° (decomp.), by $KMnO_4 \cdot H_2SO_4$.

R. S. C.

5-Alkylbarbituric acid-5-acetanilides. III. *p*-Ethoxy-derivatives. J. A. TIMM (J. Amer. Chem. Soc., 1939, 61, 2962; cf. A., 1936, 1390).—*p*- $OEt \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2Cl$ (I), the appropriate alkylbarbituric acid (1), $NaOAc$ (1.5), and NaI (0.25 mol.) in boiling 70% EtOH give 5-ethyl-, m.p. 194—205° (all m.p. with decomp.), 5-isopropyl-, m.p. 210—215°, 5-n-, m.p. 231—232°, and 5-iso-butyl-, m.p. 217—219°, 5-isoamyl-, m.p. 219—220°, and 5-allyl-, m.p. 215—218°, -barbituric acid-5-acet-*p*-phenetidine. R. S. C.

Preparation and cyclisation of monoacetylenediamines. II. S. R. ASPINALL (J. Amer. Chem. Soc., 1939, 61, 3195—3197; cf. A., 1939, II, 247).—Interaction of RCO_2Et with $(CH_2 \cdot NH_2)_2$ to give glyoxaline derivatives in ~75% yield is general, but the ease of interaction of the esters and of dehydration of the monoacylamides depends on the branching of R. The following are described. *n*-Hexo- (picrate, m.p. 93°; hydrochloride, m.p. 141°; phenylureido-derivative, m.p. 171°), α -ethyl-*n*-butyryl-, b.p. 113°/7 mm. [picrate, m.p. 123°; hydrochloride, m.p. 133°; phenylureido-derivative, dimorphic, m.p. 179° (corr.) (sinters at 150°) and 150° (corr.; rapid heating)], and phenylacet- β -aminoethylamide (picrate, m.p. 133°; hydrochloride, m.p. 142°; phenylureido-derivative, m.p. 191°). 2-*n*-Amyl-, m.p. 54° (lit. 38.8°), b.p. 108°/7 mm. [picrate, m.p. 127° (lit. 128°)], 2- α -ethyl-*n*-propyl-, m.p. 86°, b.p. 97°/9 mm. (picrate, m.p. 106°; hydrochloride, m.p. 245°; phenylureido-derivative, m.p. 133°), 2-8-methyl- α -isoamyl-*n*-hexyl-, m.p. 103°, b.p. 123°/6 mm. [picrate, m.p. 125°; phenylureido-derivative, m.p. 82°; platinichloride, m.p. (decomp.) variable], 2-benzyl-, m.p. 68°, b.p. 134°/6 mm. (picrate, m.p. 149°; hydrochloride, m.p. 174°), and 2-benzhydryl-, m.p. 137° (picrate, m.p. 185°), -4:5-dihydroglyoxaline. R. S. C.

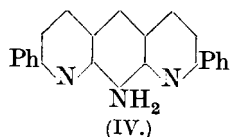
Derivatives of piperazine. XVIII. Synthesis of substituted piperazines and the hydrolysis of amines. J. P. BAIN and C. B. POLLARD (J. Amer. Chem. Soc., 1939, 61, 2704—2705).—Passing $(CH_2)_2O$ into cyclohexylamine (I) in MeOH gives cyclohexyl- β -hydroxyethyl-, b.p. 118°/10 mm., and cyclohexyldi-(β -hydroxyethyl)-amine, b.p. 175°/10 mm. When either product is heated with (I), H_2 , and Cu chromite at 250—270°/34 atm. in dioxan, it yields 20% of 1:4-dicyclohexylpiperazine, m.p. 118° (dihydrobromide), with cyclohexanol and a substance, b.p. 109—110°/10 mm. Propylene oxide with NH_2Ph or *p*- $C_6H_4Me \cdot NH_2$ in dioxan at 170° gives *NN*-di-(β -hydroxy-*n*-propyl)-aniline, b.p. 184—185°/10 mm., and -*p*-toluidine, m.p. 112°, respectively, which with (I), Cu chromite, and H_2 in dioxan yield 4-phenyl-, b.p. 205—210°/2 mm. (dihydrobromide), and 4-*p*-tolyl-1-cyclohexyl-2:6-dimethylpiperazine, b.p. 175—230°/5 mm. (monohydrobromide), respectively. With H_2 -Cu chromite in dioxan at 260—270°/34 atm., (I) gives 20% of cyclohexanol; cyclohexyldiethylamine (prepared from (I) by Et_2SO_4), b.p. 68.5—69°/10 mm., similarly gives 33% of cyclohexanol or, at 1 atm.,

much cyclohexylethylamine (NO-derivative, b.p. 127—128.5°/12.5 mm.). R. S. C.

Elimination of the acidic group from dithiocarboxylic acids. H. WUYTS and J. VAN VAERENBERGH (Bull. Soc. chim. Belg., 1939, **48**, 329—339). —RCS₂H (R = Ph, *p*- or *o*-tolyl, or α -C₁₀H₇) and *o*-C₆H₄(NH₂)₂ in Et₂O give 55—72% of 2-arylbenziminazole, but some of the acid decomposes to RH and CS₂, which latter product reacts with the amine to give 2-thiolbenziminazole. Other amines do not cause this decomp. *p*-C₆H₄Me·CS₂H with *m*-C₆H₄(NH₂)₂ in Et₂O gives *m*-NH₂·C₆H₄·NH·CS·C₆H₄Me·*p*, with *p*-NMe₂·C₆H₄·NH₂ in Et₂O gives N-*p*-dithiotoluoyl-N'-N'-dimethyl-*p*-phenylenediamine, m.p. 151°, and the anil, m.p. 145°, with *m*-NO₂·C₆H₄·NH₂ or NH₂Ph (no solvent) gives *p*-dithiotolu-*m*-nitroanilide, m.p. 154°, and -anilide, m.p. 144°, and with benzidine (I) in abs. EtOH gives impure *p*-NH₂·C₆H₄·C₆H₄·(*p*-)NH·CS·C₆H₄Me·*p* and the di-anil, m.p. 232°, or in Et₂O gives *p*-NH₂·C₆H₄·C₆H₄·NCS (II) (nearly 85%), m.p. 187° [also prepared from (I) and CS₂ in EtOH], a little [CS·NH(*p*-)·C₆H₄·C₆H₄·NH₂·*p*]₂ (III), m.p. 200°, and PhMe (68%). α -C₁₀H₇·CS₂H and (I) in boiling C₆H₆ give C₁₀H₈ (57%), (II) (62.5%), and (III) (28%). 2- α -Naphthylbenziminazole, heated rapidly, melts at 271°.

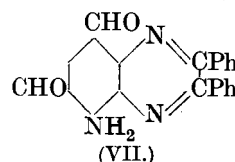
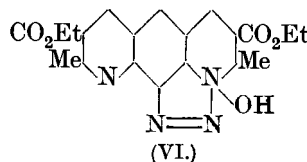
R. S. C.

Heterocyclic compounds containing nitrogen.
XLV. Nitrosation of primary amines. (Di-aminoisophthalaldehyde. III.) 4:5:6-Tri-aminoisophthalaldehyde and its condensations. P. RUGGLI and H. FREY (Helv. Chim. Acta, 1939, **22**, 1403—1412; cf. A., 1939, II, 428). —The diazotisation of 4:6-diaminoisophthalaldehyde (I) by NO·SO₄H is qualitatively established by coupling with β -C₁₀H₇·OH. (I) is transformed by NaNO₂ and conc. HCl at -10° to -15° into 5-nitroso-4:6-diaminoisophthalaldehyde (II), which softens and decomposes at ~260—273°. Attempts to acetylate the NH₂ of (II) or to condense the CHO with CH₂(CO₂Et)₂ or CH₂Ac·CO₂Et do not give useful results. Prolonged boiling with Ac₂O or alkaline reagents causes decomp. With *p*-C₆H₄Me·NH₂ in AcOH (II) gives the corresponding *ditoll*, copper-red or black-violet crystals. (II) is reduced by SnCl₂ and conc. HCl to 4:5:6-triaminoisophthalaldehyde (III), m.p. 200.5° (decomp.), obtained less readily by use of Raney Ni. (III) is insensitive to acids and has very feeble basic properties. With FeCl₃ it affords a dark violet colour which passes into a brown, amorphous ppt. (III) is readily converted into 4:6-diamino-5-acetamidoisophthalaldehyde, m.p. 293° after becoming red at 285°, but more drastic acetylation does not lead to well-defined products. (III) is transformed by PhCHO into 4:6-diamino-5-benzylideneaminoisophthalaldehyde, m.p. 156° (decomp.) after softening at 154°;



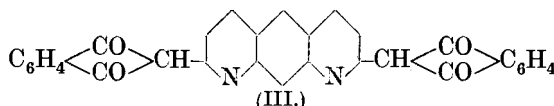
it gives a normal dioxime which darkens when heated and becomes soft at ~254°. CPhMe and KOH·MeOH convert (III) at 100° into 9-amino-2:7-dimethylbenzodipyridine (IV), red needles, m.p. 224—225°, which by prolonged contact with the mother-liquor are transformed into pale

yellow needles, m.p. 266° (decomp.). CH₂Ac·CO₂Et and NaOH·MeOH in EtOH convert (III) into Et₂ 9-amino-2:7-dimethylbenzodipyridine-3:6-dicarboxylate (V), m.p. 160° [Ac derivative, m.p. 234° (blackening) after softening at 220°], and a substance, C₁₄H₁₇O₄N₃, m.p. 201.5°. (V) is hydrolysed by alkali to the dicarboxylic acid, m.p. 318° (decomp.), which appears to be decarboxylated at 350—400° to 9-amino-2:7-dimethylbenzodipyridine. Diazotisation of (V) gives the triazolium hydroxide (VI), m.p.



195° (decomp.). (III) condenses with benzil to the quinoxaline derivative (VII), m.p. 288—289° (decomp.). H. W.

Heterocyclic compounds containing nitrogen.
XLVI. 4:6-Diaminoisophthalaldehyde. P. RUGGLI and H. FREY (Helv. Chim. Acta, 1939, **22**, 1413—1427). —Et₂ 2:7-dimethylbenzodipyridine-3:6-dicarboxylate is hydrolysed and then decarboxylated by Cu powder in quinoline at 160—230° to 2:7-dimethylbenzodipyridine (I); the yields are < those obtained by the action of conc. HCl on the ester at 130° but the process is safer. Me₂ benzodipyridine-2:7-dicarboxylate, m.p. 272° (decomp.) after becoming green at 240°, is obtained by the action of MeI on the Ag₂ salt in boiling MeOH. Benzodipyridine (II) affords a monoperchlorate, m.p. 268° after incipient decomp. at 245°, and a monomethiodide, decomp. >200°. Reduction of (II) by Na in boiling amyl alcohol gives octahydrobenzodipyridine, m.p. 111.5° (Ruggli and Staub, A., 1936, 866) [(NO)₂, m.p. 179° (decomp.), and Ac₂, m.p. 143°, derivatives]. Under similar conditions (I) affords 2:7-dimethyloctahydrobenzodipyridine, b.p. ~210°/12 mm. [hydrochloride; diperchlorate, m.p. 285—286° (decomp.); (NO)₂-derivative, m.p. 164.5°, and (?) a stereoisomeride, m.p. 151.5—152°]. (I) with *p*-NMe₂·C₆H₄·CHO in presence of piperidine at 170—175° gives 2:7-di-*p*-dimethylaminostyrylbenzodipyridine, which darkens at ~340°. With *o*-C₆H₄(CO₂)₂O and ZnCl₂ (I) gives a dark brown, amorphous product whereas with *o*-C₆H₄(CO₂Et)₂ and Na it gives the compound (III). The attempted



condensation of (I) with isoquinoline, CPhCl₃, and ZnCl₂ gives a small amount of an unidentified violet dye whilst the methiodide of (I) gives a sparingly sol. black compound with CH₂O and alkali. A brown amorphous powder results from (I) and 2-chloroquinoline. 4:6-Diaminoisophthalaldehyde (IV) and CH₂Ac·CO₂Et containing piperidine at 170° yield 7-amino-6-formyl-3-acetylcarbostyryl, characterised by its Ac derivative, decomp. 320—340°. (IV) is converted by CHO·CHNa·CO₂Et in EtOH at 30° into Et₂ 4-diaminoisophthalaldiformylacetate, m.p. 250° (decomp.) after softening at 230°, which gives the CO₂ reaction

with $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$, and Na_2 benzodipyridine-3 : 6-dicarboxylate identified by decarboxylation to (II). With boiling cyclohexanone containing a little piperidine (IV) yields 2 : 3-6 : 7-ditetramethylenebenzodipyridine, m.p. 251° after darkening (dipicrate, decomp. 195°). With $\text{CH}_2\text{Ph}\cdot\text{CN}$ and 30% NaOH in boiling EtOH (IV) gives a compound, $\text{C}_{24}\text{H}_{18}\text{N}_4$, m.p. 301° [Ac_4 derivative, m.p. $238.5\text{--}239.5^\circ$ (much decomp.)], the structure of which is not established. It is hydrolysed by conc. HCl at $140\text{--}150^\circ$ to an acid, $\text{C}_{24}\text{H}_{16}\text{O}_2\text{N}_2$ or $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_2$, m.p. 364° , which gives a *Na* salt and an *Ac* derivative, m.p. 365° . $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$, 4 : 6-dinitroisophthalaldehyde, Ac_2O , and ZnCl_2 at 80° afford *Me*, 4 : 6-dinitroisophthalaldiphenylacetate, m.p. $152.5\text{--}153.5^\circ$. H. W.

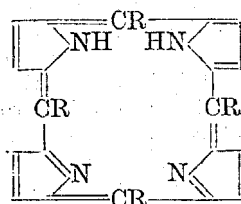
Cyclic methyleneimines. II. Hydrolysis of quaternary compounds and preparation of aliphatic secondary amines. R. BLUNDELL and J. GRAYMORE (J.C.S., 1939, 1787—1789).— $\text{NN}'\text{N}''$ -Trimethyltrimethylenetriamine (I) combines readily with *n*-alkyl iodides to give quaternary compounds, although when the reaction is slow the product is admixed with di-iodides of the base. $\text{NN}'\text{N}''$ -Trimethyltrimethylenetriamine ethiodide, m.p. 72° (decomp.), is hydrolysed (NaOH), after removal of CH_2O , to NH_2Me and NHMeEt . Similarly the *n*-propiodide, m.p. 105° (decomp.), gives on hydrolysis NHMePr^a , which with 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ forms 2 : 4-dinitrophenylmethyl-*n*-propylamine, m.p. $72\text{--}73^\circ$, and with CH_2O affords methylenebismethyl-*n*-propylamine, b.p. $170\text{--}171^\circ$. The *n*-butiodide, m.p. $123\text{--}125^\circ$ (decomp.), yields NMe_2Bu^a (hydrochloride, m.p. $183\text{--}185^\circ$; picrate, m.p. $99.5\text{--}100.5^\circ$) and NHMeBu^a (hydrochloride, m.p. 171° ; 2 : 4-dinitrophenyl derivative, m.p. 81°). (I) forms a di-iodide, m.p. 162° , and an additive product with NaI . F. R. S.

Constitution of purine nucleosides. IX. Crotonoside. R. FALCONER, J. M. GULLAND, and L. F. STORY (J.C.S., 1939, 1784—1787).—Crotonoside (I), the nucleoside of the seeds of *Croton tiglium*, L., is a *d*-riboside of isoguanine. The ultra-violet spectra of the deaminated (I) are identical with those of authentic xanthosine, and comparison of the spectra with those of 9-methylisoguanine (II) and guanosine confirms that (I) is a 9-substituted derivative, that it is not identical with guanosine, and that its aglycone is isoguanine. 2-Chloro-6-amino-9-methylpurine, prepared from the 2 : 6- Cl_2 -compound and NH_3 , with $\text{Na}\text{--EtOH}$ gives the *OEt*-compound, m.p. $252\text{--}254^\circ$ (decomp.), converted by PH_4I into (II). F. R. S.

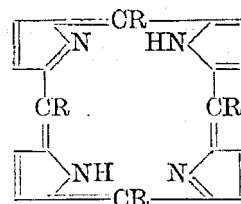
Structure of yeast ribonucleic acid, guanine-uridylic acid. R. S. TAPSON and P. A. LEVENE (Chem. and Ind., 1939, 1010).—The authors' results are misinterpreted by Gulland *et al.* (A., 1939, II, 346), whose conclusions are experimentally unjustified. R. S. C.

Porphyrins. II. Structure of the porphyrin ring system. P. ROTHEMUND (J. Amer. Chem. Soc., 1939, 61, 2912—2915).—Pyrrole and CH_2O in $\text{MeOH}\text{--C}_5\text{H}_5\text{N}$ at $140\text{--}150^\circ$ give porphyrin (HCl no. 3-3) and isoporphyrin, decomp. $>250^\circ$ (HCl no. 0-5) (*Mg*, *Cu*, and *Fe* complexes) (cf. A., 1936, 740), absorption of the latter in Et_2O being $\sim 100 \text{ \AA}$. further to the red. Isomerism is of the type (A)–(B)

($\text{R} = \text{H}$), but it is not known which formula applies to which isomeride. HCl nos. (0-5—15-7 for porphyrins and 0-075—16-8 for isoporphyrins) are listed for similar



(A.)



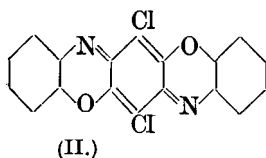
(B.)

pairs of isomerides [$\text{R} = \text{Me}$, Pr , Bu^a , Bu^b , Ph , 3 : 4 : 1- $\text{OMe}\cdot\text{C}_6\text{H}_4(\text{OH})$, *o*- and *m*- $\text{OH}\cdot\text{C}_6\text{H}_4$, and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4$], obtained from RCHO and pyrrole. R. S. C.

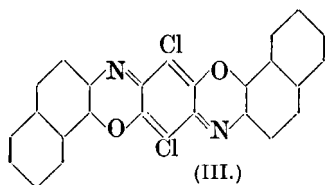
Morpholinoalkyl ethers.—See B., 1939, 1216.

Derivatives of thiolmethylamine. A. BINZ and L. H. PENCE (J. Amer. Chem. Soc., 1939, 61, 3134—3139).—When H_2S is passed into 1-hydroxymethylpiperidine (prep. from piperidine, 37% aq. CH_2O , and anhyd. K_2CO_3 at 0° , di-1-piperidinomethyl sulphide (I), m.p. $48.5\text{--}50.5^\circ$ [dihydrochloride, $+\text{H}_2\text{O}$, m.p. $171\text{--}175^\circ$ (decomp.)], is obtained. If cooling is omitted, 1-thiolmethylpiperidine (II), m.p. $12.5\text{--}15^\circ$ (hydrochloride, $+0.5\text{H}_2\text{O}$, m.p. $195\text{--}205^\circ$), is obtained exothermally, probably by way of (I). 4-Hydroxymethylmorpholine (similarly prepared from 1 mol. each of morpholine and CH_2O at 0° gives di-4-morpholinomethyl sulphide, m.p. $105\text{--}108^\circ$, and 4-morpholinomethyl thiolmethyl sulphide, $+0.5\text{H}_2\text{O}$, amorphous, m.p. $72\text{--}82^\circ$; at 55° in presence of conc. HCl (not in its absence) there are formed 4-thiolmethylmorpholine (III), m.p. $86\text{--}88^\circ$, and $\alpha\eta$ -di-4-morpholino- $\beta\delta\zeta$ -trithia-*n*-heptane, $\text{S}(\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{N} < \begin{smallmatrix} [\text{CH}_2]_2 \\ [\text{CH}_2]_2 \end{smallmatrix} > \text{O})_2$, amorphous, m.p. $\sim 77\text{--}84^\circ$, the latter being the main product if an excess of CH_2O is used and being probably produced from $(\text{OH}\cdot\text{CH}_2)_2\text{S}$. Formation of the polymeric compounds is more pronounced with $\text{NH}([\text{CH}_2]_2\cdot\text{OH})_2$, for, after condensation with CH_2O at 0° , H_2S gives an amorphous substance, $(\text{OH}\cdot[\text{CH}_2]_2)_2\text{N}\cdot[\text{CH}_2\cdot\text{S}]_n\cdot\text{H}$, m.p. $\sim 224\text{--}226^\circ$ (melts if immersed in a bath at 170° , resolidifies, remelts at $218\text{--}228^\circ$), but use of an excess of CH_2O and passing H_2S at 65° gives a substance ($\text{N} : \text{S} : \text{I} : 14 : 4$), m.p. $230\text{--}233^\circ$. At $150\text{--}170^\circ/4 \text{ mm}$. (II) gives dipiperidinomethane and an amorphous substance ($\text{S} 58.4\%$), m.p. $228\text{--}231^\circ$. With dil. HCl at 90° , (II) gives $(\text{CH}_2\text{S})_3$. With $\text{HgCl}_2\text{--EtOH}$, (II) or (III) gives *Hg* di(thiolmethyl) ether, $\text{Hg} < \begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{S} \end{smallmatrix} > \text{O}$, decomp. $95\text{--}105^\circ$ (with H_2S in H_2O gives HgS immediately), probably by way of $\text{Hg}(\text{S}\cdot\text{CH}_2\cdot\text{OH})_2$. With $\text{Cu}(\text{OAc})_2\text{--EtOH}$, (II) or (III) gives *Cu* methylene dimercaptide, $\text{Cu} < \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{S}$, decomp. $105\text{--}110^\circ$ [with aq. Na_2S (not H_2S) gives CuS], probably by way of $\text{Cu}(\text{S}\cdot\text{CH}_2\cdot\text{OH})_2$ and $\text{O} < \begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{S} \end{smallmatrix} > \text{Cu}$. (I) and (II) in H_2O are toxic to paramacia and *Daphnia*. Most of the above S compounds, when injected intravenously, are highly toxic to mice. R. S. C.

Triphenyldioxazines. H. E. FIERZ-DAVID, J. BRASSEL, and F. PROBST (Helv. Chim. Acta, 1939, **22**, 1348—1358).—Gradual addition of o -NH₂·C₆H₄·OMe to chloranil and anhyd. NaOAc in o -C₆H₄Cl₂ and subsequent boiling of the mixture gives 2 : 5-dichloro-3 : 6-di- o -anisidino- p -benzoquinone (I), converted by



anhyd. AlCl₃ in dry C₆H₅N at 80—90° into 9 : 10-dichloro-triphenyldioxazine (II) (no distinct m.p.). This is also obtained when (I) is replaced by the NHPH- or o -phenetidin-derivative. With the latter or with (I) condensation can be effected with PhNO₂ in presence or absence of FeCl₃. With the NHPH-derivatives only traces of (II) are obtained by this method. With BzCl or p -C₆H₄Me·SO₂Cl in PhNO₂ the yields are satisfactory if not quant. 3 : 7 : 9 : 10-Tetrachlorotriphenyldioxazine and 9 : 10-dichloro-2 : 6-dinitrotriphenyldioxazine are obtained similarly; the latter substance is also derived from 5 : 1 : 2-NO₂·C₆H₃(OH)·NH₂. It is reduced by Na₂S₂O₄ and alkali to the diaminodihydro-compound, oxidised by H₂O₂ to 9 : 10-dichloro-2 : 6-diaminotriphenyldioxazine. 9 : 10-Dichloro-3 : 7-dinitro- and -3 : 7-diamino-triphenyldioxazine are obtained similarly. 9 : 10-Dichloro-1 : 3 : 5 : 7-tetranitrotriphenyldioxazine is obtained by the action of conc. H₂SO₄ on the diarylquinone from chloranil and picramic acid. 9 : 10-Dichloro-2 : 6-dibenzamido-3 : 7-dimethyltriphenyldioxazine is obtained by boiling the condensation product of chloranil and 4-benzamido-2-methoxy-5-methylaniline with BzCl in PhNO₂. 9 : 10-Dichloro-3 : 7-diethoxy- and -3 : 7-dimethoxy-triphenyldioxazine are described. The



condensation product from chloranil and β -C₁₀H₇·NH₂ is readily cyclised to 9 : 10-dichloro-2 : 3 : 5 : 6-dibenzotriphenyldioxazine (III). Chloranil, α -C₁₀H₇·NH₂, and anhyd. NaOAc in boiling EtOH afford 3 : 6-dichloro-2 : 5-di-1'-naphthylamino-1 : 4-benzoquinone, which passes in boiling PhNO₂ into 9 : 10-dichloro-3 : 4 : 7 : 8-dibenzotriphenyldioxazine. The following are described : 9 : 10-dichloro-2 : 6-dibenzeneazo-3 : 4 : 7 : 8-dibenzotriphenyldioxazine by condensing chloranil with 4 : 1-PhN₂·C₁₀H₆·NH₂ in EtOH and cyclisation of the product with p -C₆H₄Me·SO₂Cl in PhNO₂; 9-chloro-2 : 6 : 10-trianilino-triphenyldioxazine from (II) and NH₂Ph·HCl in boiling NH₂Ph; 9 : 10-dichloro-2 : 6-dianilino-triphenyldioxazine, by treating the condensation product of chloranil and "1-amino-2-methoxydiphenylamine" in o -C₆H₄Cl₂ with AlCl₃ in C₆H₅N.

H. W.

Ox- and thi-azoles (anthraquinone series).—See B., 1939, 1219.

spiroDithiohydantoins.—See B., 1939, 1216.

Cyanine dyes.—See B., 1939, 1220, 1297.

Erythrophleum alkaloids. I. Cassaine, a crystalline alkaloid from the bark of Erythrophleum guineense (G. Don). G. DALMA (Helv.

Chim. Acta, 1939, **22**, 1497—1512).—The powdered bark of *E. guineense*, obtained from the Congo mouth forests, is moistened with 10% NH₃ and exhaustively extracted with Et₂O, thereby giving cassaine (I), C₂₄H₃₉O₄N, m.p. 142.5°, [α]_D²⁰ −111° in 95% EtOH, −103° in abs. EtOH, −117° in 0.1N-HCl, which is best isolated through the *H* sulphate (+2H₂O), m.p. ~29° (decomp.). (I) can be sharply titrated with iodoeosin, Me-red, or bromophenol-blue as indicator. The hydrochloride (+1H₂O) has m.p. 212—213° (vac.). The formation of cassaine acetate, m.p. 123—124°, and cassaine oxime, m.p. 123—125°, establishes the nature of 2 O. (I) is hydrolysed by boiling N-HCl to cassaic acid (II), C₂₀H₃₀O₄, m.p. 203°, [α]_D²⁰ −126.3° in 95% EtOH, and a base {identified by Faltis and Holzinger (A., 1939, II, 459) as NMe₂·[CH₂]₂·OH}. Alkaline hydrolysis of (I) affords allocassaic acid, m.p. 222—224°, [α]_D²² +81.8° in 95% EtOH. Me cassate, m.p. 189—190°, gives an acetate, m.p. 189—191° (semicarbazone, m.p. 246—247°). Oxidation of (II) by CrO₃ in AcOH at 35° yields dehydrocassaic acid (III), m.p. 238—239°, [α]_D²⁰ −164.5° in 95% EtOH [Me ester, m.p. 129—130°, and its dioxime, m.p. 130—132°, and disemicarbazone, m.p. 290° (decomp.)]. Attempted reduction (Clemmensen) of (III) causes extensive decomp. (I) could not be isolated from a sample of *E. guineense* from the Central Congo, which contained ~0.5% of an amorphous base very similar to Harnack's and technical erythrophleine. A third sample of bark from the mouth of the Congo appeared to be derived from a different sub-species and contained ~0.1% of alkaloid of which ~10% was (I). H. W.

Erythrophleum alkaloids. II. Carbon skeleton and position of the double linking in cassaic acid. L. RUZICKA and G. DALMA (Helv. Chim.

Acta, 1939, **22**, 1516—1523).—The absorption spectrum shows that the double linking is in the $\alpha\beta$ position to CO₂H in cassaic acid (I), cassaine (II), and Me₂ diketocassinate. The presence of a double linking $\alpha\beta$ to CO is unlikely. (For the OH- and CO-free, saturated parent acid of (I) the name "cassanic acid" is proposed.) allocassaic acid does not show the band characteristic of $\alpha\beta$ -unsaturated acids and the unsaturated linking is probably displaced to the $\beta\gamma$ -position during alkaline hydrolysis; the characteristic CO band is present. Dihydrocassanic acid (III) does not show any absorption between 2000 and 3400 Å., confirming the reduction of the erstwhile CO and saturation of the double linking. Hydrogenation of (II) (PtO₂ in AcOH or Raney Ni in EtOH) gives dihydrocassaine, m.p. 115—116°, [α]_D²⁰ 0° ± 2° in 95% EtOH, −6.5° ± 1° in 0.1N-HCl, converted by KOH-EtOH into hydroxyketocassanic acid, m.p. 253—255°, [α]_D²⁰ 0° ± 2° in 95% EtOH, −5° ± 1° in 0.1N-NaOH, also obtained by hydrogenation of (I). It is reduced by Na and EtOH to (III), m.p. 262—265°, [α]_D²⁰ −7° ± 1° in 0.1N-NaOH (Me ester, m.p. 172—174°). Dehydrogenation of (III) by Se in an open vessel at 340° affords 1 : 7 : 8-trimethylphenanthrene (IV), m.p. 142—143° [picrate, m.p. 133—135°; additive compound with C₆H₃(NO₂)₃, m.p. 192—193°]. The similar action in a sealed tube at 340° leads to (IV) and (?) the non cryst. 1 : 7 : 8-trimethyltetrahydrophenanthrene (V), characterised by its compound

with $C_6H_3(NO_2)_3$, m.p. 85—88°. (IV) is transformed into (III). All m.p. are corr. H. W.

Erythrina alkaloids. V. Constitution of erythramine. K. FOLKERS and F. KONIUSZY (J. Amer. Chem. Soc., 1939, **61**, 3053—3055).—Erythramine (I) (hydriodide, m.p. 249°, $[\alpha]_D^{20} + 220^\circ$) (A., 1939, II, 349) contains 1 OMe and CH_2O_2 , but no CMe, NAlk, or OH (indifferent to Ac_2O and $BzCl$). The N is *tert.*, as $Mel-MeOH$ gives a *methiodide*, m.p. 96—98°, $[\alpha]_D^{25} + 176^\circ$ in H_2O . H_2-PtO_2 in very dil. HCl at 2 atm. converts (I) (not its hydriodide in H_2O) into a *tert.* H_2 -derivative, m.p. 89—90° [*hydriodide*, +solvent, m.p. 214—215° (decomp.), α_D 0 in H_2O ; *hydrobromide*, + H_2O (retained at 140°/2 mm.), m.p. 240°; *methiodide*, +0.5 H_2O , m.p. 160—161°]. The N is thus common to two rings. (I) is probably tetracyclic. (I) has curare-action (frog) at 7 mg. of hydrobromide per kg., the *methiodide* and H_2 -derivative being one fifth and one thirtieth, respectively, as active. R. S. C.

Structure of monocrotaline, the alkaloid in *Crotalaria spectabilis* and *C. retusa*. I. R. ADAMS and E. F. ROGERS. II. **Monocrotic acid obtained by alkaline hydrolysis of the alkaloid.** R. ADAMS, E. F. ROGERS, and F. J. SPRULES. III. **Monocrotalic acid.** R. ADAMS, E. F. ROGERS, and R. S. LONG (J. Amer. Chem. Soc., 1939, **61**, 2815—2819, 2819—2821, 2822—2824).—I. Monocrotaline (isolation from *C. spectabilis* and *C. retusa* seeds described), new formula $C_{16}H_{23}O_6N$, m.p. 197—198° (decomp.), $[\alpha]_D^{25} - 54.7^\circ$ to -55.7° in $CHCl_3$ [*hydrochloride*, m.p. 184° (decomp.), $[\alpha]_D^{25} - 38.4^\circ$ in H_2O ; *methiodide*, +3 $MeOH$, m.p. 205° (decomp.), $[\alpha]_D^{25}$ (anhyd.) +23.4° in $MeOH$], resembles the *Senecio* alkaloids. With boiling, aq. $Ba(OH)_2$ it gives retronecine and *monocrotic acid* (I), $C_7H_{12}O_3$, b.p. 145—146°/18 mm., α 0 (*p-bromophenacyl* ester, m.p. 78°). With H_2-PtO_2 at 2—3 atm. in $AcOH$ it gives retronecanol, m.p. 95—96°, $[\alpha]_D^{25} - 91.1^\circ$ in $EtOH$ [*hydrochloride*, m.p. 210° (decomp.)]; *methiodide*, m.p. 193° (decomp.), $[\alpha]_D^{27} - 52.8^\circ$ in $MeOH$; *picrate*, m.p. 210°, and *monocrotalic acid* (II), $C_8H_{12}O_5$, m.p. 181—182°, $[\alpha]_D^{25} - 5.33^\circ$ in H_2O . (II) is a *lactonic acid*, converted by boiling 10% $NaOH$ into (I) and CO_2 . M.p. are corr.

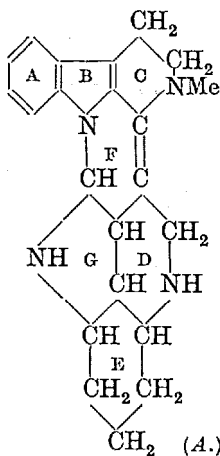
II. With CH_2N_2 or H_2SO_4-MeOH , *monocrotic acid* (I) gives a *Me* ester, b.p. 94—96°/18 mm. (2 : 4-*dinitrophenylhydrazones*, m.p. 95—96°). With $I-NaOH$, (I) gives CHI_3 , and with $NaOBr$ gives *dl.* and *meso.* $(CHMe.CO_2H)_2$. At 240—250° (I) gives $\alpha\beta\gamma$ -*trimethylangelicalactone* (III), b.p. 121°/20 mm. (positive tests with Tollens' and Legal's reagents), hydrolysed to (I) by 10% $KOH-EtOH$ and hydrogenated (Raney Ni; Et_2O ; 120°/133 atm.) to $\alpha\beta$ -*dimethyl- γ -valerolactone*, b.p. 106—107°/20 mm., obtained also by hydrogenating (I). It is concluded that (I) is $\alpha\beta$ -*dimethyl-lævulic acid*.

III. *Monocrotalic acid* (II) is shown to be γ -*hydroxy- α -carboxy- $\alpha\beta$ -dimethyl- γ -valerolactone*. With CH_2N_2 (not $MeOH$ -acid; proof of *tert.*- CO_2H) it gives a *Me* ester, m.p. 79—80°, $[\alpha]_D^{30} - 16.24^\circ$ in abs. $EtOH$ (1 active H), which at 200—210° gives (II) and *Me anhydromonocrotalate* [α -*carbomethoxy- $\alpha\beta\gamma$ -trimethylangelicalactone*] (IV), b.p. 115—116°/3 mm., hydro-

lysed to (III), which is also obtained with CO_2 and H_2O from (II) at 200°. Hydrogenation (Raney Ni; Et_2O ; 125°/167 atm.) of (IV) gives α -*carbomethoxy- $\alpha\beta$ -dimethylvalerolactone*, b.p. 115—117°/1 mm., $[\alpha]_D^{25} + 5.60^\circ$ (homogeneous), hydrolysed to the *lactonic acid*, m.p. 131—132°, $[\alpha]_D^{30} + 3.80^\circ$ in abs. $EtOH$ (*p-bromophenacyl* ester, m.p. 142—143°, $[\alpha]_D^{30} - 3.89^\circ$ in $COMe_2$). M.p. are corr. R. S. C.

Calycanthine. IV. Structural formula.

R. H. F. MANSKE and L. MARION (Canad. J. Res., 1939, **17**, B, 293—301).—The structure (A) is assigned to calycanthine (I) since it is converted into *N*-methyltryptamine by comparatively mild treatment, it gives quinoline when treated with P and HI, it is degraded by Se to norharman, calycanine (II), 3-methyl- and 3-ethyl-indole, and lepidine, it does not contain CMe, and it gives NH_3 when distilled with Pd in N_2 . Additional support for the introduction of the fourth N as in ring G is that benzoylation easily severs the N-C linking from rings B to G. Benzoylation yields *benzoyl-N*-methyltryptamine (III) and an amorphous



acid, m.p. 170—174°, which contains N and one or more Bz groups and gives an amphoteric substance when debenzoylated and quinoline (IV) when heated with Se. It is probably a largely hydrogenated 5(?)-aminoquinoline-3 : 4-dicarboxylic acid in which the N are lactamised or benzoylated. When treated with Se (III) does not yield (IV). (I) is recovered unchanged after treatment with Na and Bu^oOH so that most double linkings must be presumed to form part of aromatic rings. When oxidised by Gadamer's method (I) loses 2 H, which can be readily re-added by reduction; since the product so obtained is identical with (I) no stereoisomeric change appears to be involved and the 2 H concerned are probably removed from the two CH_2 of ring c. (II) is probably $C_{16}H_{10}N_2$ although the mol. wt. agrees with the doubled formula. It does not give Ehrlich's reaction. Possible formulae are discussed. (I) has also been isolated from *Calycanthus occidentalis*, Hook. et Arn., and from *C. glaucus*, Willd (*C. fertilis*, Walt.). The constitution assigned to (I) by Barger *et al.* (A., 1939, II, 291) is adversely criticised. H. W.

Constitution of solasonine (solanine-s). L. H. BRIGGS (Nature, 1939, **144**, 247—248).—Additional analyses of solasonine (I) and solasodine (II) agree with the formulae $C_{45}H_{73}O_{16}N$ and $C_{27}H_{43}O_8N$, respectively. A cryst. Ac_1 derivative, m.p. 195°, of (II) has been isolated. (II) yields quaternary salts by simple addition [*methiodide*, m.p. 286° (decomp.); *ethiodide*, m.p. 284° (decomp.)]. NMe is absent. It adds H and Br. A constitutional formula is suggested. (II) is probably a OH-derivative of solanidine (III). (II) and (III) give a series of colour reactions with *p*-substituted aldehydes and $AcOH-H_2SO_4$.

[With R. C. BELL.] Purapurine from the fruit of

Solanum aviculare, but not the alkaloid from *S. auriculatum*, is identical with (I). L. S. T.

Di-*p*-aminophenylarsinic acid. G. GILTA (Bull. Soc. chim. Belg., 1939, 48, 444—446).— p - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ (I) (80 g.) and NH_2Ph (500 g.) at 220° give (p - $\text{NH}_2\cdot\text{C}_6\text{H}_4$) $_2\text{AsO}_2\text{H}$ (crystallography described), from which unchanged (I) is removed by dissolution in aq. NaOAc . R. S. C.

Intramolecular substitution as a means of comparing activating and deactivating effects. (Miss) J. D. C. MOLE and E. E. TURNER (J.C.S., 1939, 1720—1724).—The measurement of rates of ring-closure of substituted *o*-phenoxyphenyldichloroarsines into 10-chlorophenoxarsines shows that the "internal" electrophilic reagent places activated and deactivated centres in aromatic systems in the same order as that given by an external reagent such as HNO_3 . The following are described: 2-nitro-2'-methyl-, m.p. 39 — 40° , -3':5'-dimethyl-, m.p. 63 — 64° , -2':5'-dimethyl-, b.p. 234 — $235^\circ/44$ mm., -2':4'-dimethyl-, m.p. 61 — 62° , and -4'-methoxy-, m.p. 75 — 76.5° , 2-amino-3':5'-dimethyl-, m.p. 56 — 57° , -2':5'-dimethyl-, b.p. 213 — $214^\circ/44$ mm., -2':4'-dimethyl-, m.p. 64 — 65° , and -4'-methoxy-diphenyl ether, b.p. 212 — $213^\circ/21$ mm.; 2-o-, m.p. 184 — 185° , and 2-m-tolyl-, m.p. 193 — 194° , 2-(3':5'-dimethylphenoxy)-, m.p. 178 — 179° , 2':5'-, m.p. 177.5 — 178° , and 2':4'-dimethyl-, m.p. 184 — 185° , 2-p-anisoyloxy-, m.p. 188 — 189° , and 2-p-bromophenoxy-phenyl-arsinic acid, m.p. 183 — 184° ; 2-o-, m.p. 73 — 74° , 2-m-, and 2-p-tolyl-, m.p. 73° , 2-(3':5'-, m.p. 71.5 — 73° , 2-(2':5'-, m.p. 70 — 71.5° , and 2-(2':4'-dimethylphenoxy)-, m.p. 52.5 — 54° , 2-p-anisoyloxy-, m.p. 63 — 64° , and 2-p-bromophenoxy-phenyldichloroarsine, m.p. 76 — 77° ; 10-chloro-4-, m.p. 90 — 91° , and -3-methyl-, m.p. 140 — 141° (also prepared from 2-amino-5-methyldiphenyl ether, b.p. 213 — $214^\circ/55$ mm.), -1:3-, m.p. 138 — 139° , -1:4-, m.p. 146 — 147° , and -2:4-dimethyl-, m.p. 130 — 131° , -2-methoxy-, m.p. 108 — 109° , and -2-bromo-phenoxarsine, m.p. 172 — 173° . F. R. S.

Co-ordination complexes of the mercuric ion with cyclohexene. H. J. LUCAS, F. R. HEPNER, and S. WINSTEIN (J. Amer. Chem. Soc., 1939, 61, 3102—3106).—It is shown, mainly by distribution between CCl_4 and $\text{Hg}(\text{NO}_3)_2\text{--KNO}_3\text{--H}_2\text{O}$ (method modified from that of Winstein *et al.*, A., 1938, II, 224), that cyclohexene rapidly undergoes reversible co-ordination to yield complexes X_2Hg^{++} and $\text{X}_2\text{Hg}(\text{OH})^+$. These complexes are typical of org. intermediates, the existence of which is often assumed but not demonstrable, and they are of importance in mercuration reactions. R. S. C.

Fluorinated aromatic mercurials. M. F. W. DUNKER and E. B. STARKEY (J. Amer. Chem. Soc., 1939, 61, 3005—3007).— $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ with $\text{HNO}_2\text{--HBF}_4$ gives $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{BF}_4$ (*o*- 92, *m*- 92, *p*- 100%), yielding by thermal decomp. in sand $\text{C}_6\text{H}_4\text{F}\cdot\text{NO}_2$ (*o*- 13, *m*- 43, *p*- 58%), which are reduced (Sn--HCl) to $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ (*o*- 70, *m*- 89, *p*- 75%; 100% of *p*-compound formed by $\text{H}_2\text{--Pd--C}$ in 95% EtOH). This then yields $\text{C}_6\text{H}_4\text{F}\cdot\text{N}_2\cdot\text{BF}_4$ (*o*- 70, *m*- 98, *p*- 86%) and thence ($\text{SnCl}_2\text{--HgCl}_2$) *o*- (I) (24%), m.p. 159 — 160° (corr.), *m*- (28%), m.p. 250 — 251° (corr.) (lit. 243°), and *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{HgCl}$ (24%), m.p. 293 — 294°

(decomp.; corr.) (lit. 291°). PhF and $\text{Hg}(\text{OAc})_2$ in boiling AcOH give 11% of (I). p - $\text{C}_6\text{H}_4\text{F}\cdot\text{OH}$ (prep. from p - $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ or by AlCl_3 from p - $\text{C}_6\text{H}_4\text{F}\cdot\text{OEt}$), $\text{Hg}(\text{OAc})_2$, and a little AcOH in H_2O at room temp. give much 5-fluoro-2-hydroxyphenylmercuriacetate, m.p. 193 — 194° (decomp.), and a little impure dimercurial. p - $\text{C}_6\text{H}_4\text{F}\cdot\text{CO}_2\text{H}$ (from p - $\text{C}_6\text{H}_4\text{MeF}$ in 58% yield by KMnO_4) gives a poor yield of 4-fluoro-2-chloromercuribenzoic acid (II), m.p. 240 — 241° (decomp. from 230°). 4-Fluoro-3-aminobenzoic acid, (prep. in 98% yield from the NO_2 -acid by $\text{H}_2\text{--Pd}$), m.p. 182 — 183° (decomp.) [hydrochloride, m.p. 240 — 243° (decomp. from 215°); *Ac* derivative, m.p. 245 — 246° (decomp.; rapid heating), 200° (decomp.; slow heating)], gives a diazonium borofluoride, decomp. 185° , and thence a little (II). R. S. C.

Mercuri-derivatives of acids.—See B., 1939, 1295.

Preparation of seleno-*o*- and -*m*-cresol. D. G. FOSTER (J. Amer. Chem. Soc., 1939, 61, 2972—2973).— $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgHal}$ and Se in H_2 (not air) give *o*-, b.p. $99^\circ/25$ mm., and *m*-selenocresol, b.p. $89^\circ/16$ mm. (*Cu* salts), oxidised by HNO_3 to *o*-, m.p. 123 — 125° , and *m*-tolylselenious acid, m.p. 118 — 119° . R. S. C.

Simplified procedure for isolation of lysine from protein hydrolysates. E. E. RICE (J. Biol. Chem., 1939, 131, 1—4).—The method, which involves direct pptn. of the lysine as picrate, is described. After hydrolysis of the protein with dil. H_2SO_4 and removal of the latter with $\text{Ba}(\text{OH})_2$, the liquid is conc. and, after removal of the insol. NH_2 -acids, excess of picric acid is added. The process greatly reduces the time required for isolation of lysine and eliminates the electrolysis which is an essential part of the method of Cox *et al.* (A., 1929, 686). The yield and quality of lysine monohydrochloride prepared by the process are as high as those obtained after electrolysis. Histidine can be separated as a by-product in the method, which can be used with hydrolysates that have been neutralised with $\text{Ca}(\text{OH})_2$ instead of $\text{Ba}(\text{OH})_2$. J. N. A.

Thiol groups in proteins. Effect on ovalbumin of various salts of guanidine.—See A., 1939, III, 1095.

Interaction of casein with aqueous solutions of aniline and pyridine. A. J. KOROLEV and V. A. VILENSKI (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 266—269; cf. A., 1936, 1199).—Results are discussed in terms of solvation. A. T. P.

Determination of carbon-oxygen equivalence and empirical formula by iodic acid oxidation. B. E. CHRISTENSEN and J. F. FACER (J. Amer. Chem. Soc., 1939, 61, 3001—3005).—10—20 mg. of an org. substance are oxidised by $\text{KIO}_4\text{--H}_2\text{SO}_4$ at $190 \pm 5^\circ$ (or $>200^\circ$, if necessary). The O_2 consumed is determined from the residual HIO_4 (a blank is essential). The CO_2 is absorbed in $\text{Ba}(\text{OH})_2$ and determined by titration. Thence the empirical formula is calc. Apparatus and technique of all operations are detailed. The effect of N, halogen, and S was not investigated. R. S. C.

Elementary micro-analysis. A. F. RICHTER (Časop. Českoslov. Lék., 1937, 17, 288—294).—Friedrich's method (cf. A., 1935, 1515) is recommended for elementary micro-analysis especially

where analyses are made only periodically. Various absorption reagents have been tested and sources of error are stated. Fe and P if present in an org. mol. in the ratio 1:1 can be determined precisely. The loss of traces of C depending on the nature of the ash is confirmed. Check determinations using new means of absorption lower the final error. F. R.

Determination of halogens in organic material. O. TOMČEK and K. PETÁK (Časop. Českoslov. Lék., 1937, 17, 309—326).—New methods (use of Ca and Li metals; oxidation in alkaline medium) and modified known methods for the determination of halogens in org. matter are examined, and those convenient for certain groups of compounds or general use are discussed. Decomp. by Na and K are good general methods but the best is catalytic hydrogenation with Pd completed by simultaneous reduction with $N_2H_4 \cdot H_2SO_4$. F. R.

Micro-iodometric determination of nitrogen. S. M. STREPKOV (Ann. Chim. Analyt., 1939, 21, [iii], 257—260).—The determination is based on the reaction $2NH_4^+ + 2OH^- + 3OBr^- = 3Br^- + 5H_2O + N_2$, and iodometric titration of the excess of NaOBr. The sample (0.1—2.5 mg. of N) is heated with 1 c.c. of conc. H_2SO_4 , and H_2O_2 is added at intervals until conversion of N into $(NH_4)_2SO_4$ is complete. The H_2SO_4 solution is diluted accurately to 25 c.c., and 10 c.c. are treated with 3 c.c. of 0.1N-KBrO₃ and 1 c.c. of 10% aq. KBr. After shaking to liberate Br completely, 3—3.2 c.c. of 5N-NaOH are added, when the above reaction takes place. The excess of OBr⁻ is determined by addition of 1 c.c. of 10% KI, 3—3.5 c.c. of 5N-HCl, and titration with 0.01N- $Na_2S_2O_3$ after keeping for 20 min. Test data for glycine, NH_2Ph , $OH \cdot C_6H_4 \cdot NO_2$, tyrosine, and the roots of *Biebersteinia multifida* are recorded. L. S. T.

Titrimetric determination of organic substances by chromic oxidation. Use of stable nitro-chromic solutions. H. CORDEBARD (J. Pharm. Chim., 1939, [viii], 30, 263—272).—A solution of $K_2Cr_2O_7$ in conc. HNO_3 is stable and readily oxidises a wide range of compounds at room temp., at 100°, or at its b.p. (122°). Cyclic compounds are oxidised with difficulty and AcOH does not lose CO_2 . Cu, NO_2 , and NO can be determined. After brief contact of a solution containing EtOH with standard $K_2Cr_2O_7$ -conc. HNO_3 , followed by treatment with KI, the I liberated ($Na_2S_2O_3$ titration) is a measure of the EtOH content. EtOH is determined similarly in presence of $CHCl_3$ or camphor. It must be first freed from oxidisable substances. J. L. D.

Microchemical technique. III. Semi-micro-preparation and purification of organic substances. G. F. WRIGHT (Canad. J. Res., 1939, 17, B, 302—307).—The apparatus described is designed for (1) evaporating liquid from a microscope slide without undue spreading, (2) the delivery of drops of clean reagents, (3) crystallisation in a side-arm test-tube modified so as to eliminate contamination of the stopper when the liquid is decanted through the side-arm, (4) filtration by a Pyrex filter with sealed-in porcelain disc, and (5) distillation by a modification of the method of Benedetti-Pichler and Schneider. H. W.

Determination of the branched isomerides in mixtures of paraffin hydrocarbons. U. VON WEBER (Angew. Chem., 1939, 52, 607—610).—A distillation apparatus with a column 4.2 m. long and filled with Raschig rings 4 mm. long and 4 mm. in diameter is described, which permits the separation of oils into the *n*-paraffins and fractions of intermediate b.p., containing all the branched isomerides. To determine the degree of branching in a mixture of paraffins, the latter is separated into fractions which distil over between temp. 5° > the b.p. of the successive *n*-paraffins. The total wt. (G_n), mean mol. wt. (M_n), and b.p. (T_n) of each fraction are then determined. By assuming that Raoult's law holds for the mixtures and that the b.p. of the *n*-hydrocarbon (T_0) is lowered by 7° for each branch in the chain, it is shown that the degree of branching in each fraction (Z_n) is given by $(T_0 - T_n)/7.0$, and the total degree of branching in the mixture is given by $\Sigma Z_n \times (G_n/M_n) \times \Sigma M_n / \Sigma G_n$. J. W. S.

Rapid determination of halogen in hydrocarbons substituted by chlorine and fluorine. W. D. TREADWELL and M. ZÜRCHER (Helv. Chim. Acta, 1939, 22, 1371—1380).—Determination of halogen in CCl_2F_2 by decomp. with an excess of air in contact with red-hot CaO is inconvenient. Treatment of CCl_2F_2 with Na in liquid NH_3 followed by decomp. of excess of Na by NH_4NO_3 enables Cl⁻ to be determined argentometrically but the determination of F⁻ by $FeCl_3$ with electrometric measurement of the end-point is impeded by the presence of a small amount of $NaNO_2$ formed during the decomp. of NH_4NO_3 and by a flattening of the titration curve by the NH_4 salt present. Combustion of hydrocarbons containing Cl and F in a H_2 flame containing a 100-fold excess of H_2 causes almost complete conversion of halogen into H halide. To obviate all loss, so much H_2O vapour is supplied to the flame that the acid solutions obtained by condensation of the products of combustion are ~0.1N. Traces of free Cl_2 are formed in the flame (from the amount of which it is attempted to calculate the energy of activation of the Deacon reaction). A special burner is described. Condensation of the reaction products is simply effected by allowing the flame to burn in a small cavern in a lump of pure ice. Alternatively, the products are brought in contact with a cooled glass tube, and SiO_2 is removed prior to the determination of F⁻ in the condensate, or the flame is allowed to burn inside a steam-heated bell and the products are drawn through a sintered glass plate into dil. alkali. H. W.

Determination of ethyl alcohol in presence of methyl alcohol, isopropyl alcohol, and acetone. E. J. BOORMAN (Analyst, 1939, 64, 791—794).—When the sample is treated with an excess of $HgSO_4$ - $K_2Cr_2O_7$ reagent, $COME_2$ is pptd., Pr^oOH is oxidised to $COME_2$ and pptd., $MeOH$ is oxidised to CO_2 and H_2O , and $EtOH$ is oxidised to AcOH. The AcOH is distilled in steam and titrated. The $HgCr_2O_7$ compounds are highly explosive when dry.

E. C. B. S.

Polarographic method in organic chemistry. I. Electro-reduction of peroxides.—See A., 1939, I, 624.

Identification and determination of hexoses in polysaccharides.—See A., 1940, III, 84.

Determination of nitrogen as ammonia in monosubstituted carbamides, carbamates, allophanates, and semicarbazones. S. ROVIRA (Compt. rend., 1939, 209, 754—757; cf. A., 1939, II, 526).—When the compounds (listed) are boiled with 20% KOH-glycerol for up to 2 hr., all or a const. fraction of the contained N is converted into NH_3 ; the error is (usually) small. The method can be adapted as a micro-method. J. L. D.

Azides as reagents for the identification of organic compounds. XV. 2:6-Dinitro-*p*-toluazide as reagent for identification of amines. P. P. T. SAH (Rec. trav. chim., 1939, 58, 1008—1012; cf. A., 1939, II, 398).—2:6-Dinitro-*p*-tolylcarbamyl derivatives of the following are described: NH_2Ph , m.p. 221°; *o*-, m.p. 231°, *m*-, m.p. 220°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 233° (decomp.); 1:3:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2$, m.p. 233—234° (decomp.); *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$, m.p. 233°; α -, m.p. 260° (decomp.), and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 253—254° (decomp.); *o*-, m.p. 254° (decomp.), *m*-, m.p. 239—240°, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, m.p. 242—243°; *o*-, m.p. 257° (decomp.), *m*-, m.p. 235°, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, m.p. 232—233° (decomp.); *o*-, m.p. 264—265° (decomp.), *m*-, m.p. 246—247° (decomp.), and *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{NH}_2$, m.p. 260—261° (decomp.); *o*-, m.p. 258—260°, *m*-, m.p. 278—279°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, m.p. 245° (decomp.); 3-chloro-, m.p. 237—238° (decomp.), -bromo-, m.p. 246° (decomp.), and -iodo-4-, m.p. 246° (decomp.); 6-chloro-, m.p. 270—271° (decomp.), -bromo-, m.p. 259° (decomp.), and -iodo-3-, m.p. 281—282° (decomp.); and 5-chloro-, m.p. 228—229°, -bromo-, m.p. 240°, and -iodo-2-aminotoluene, m.p. 254—255° (decomp.); 4:1:2-, m.p. 286—287° (decomp.), 4:1:3-, m.p. 198°, 3:1:6-, m.p. 279—280° (decomp.), 3:1:4-, m.p. 234—235° (decomp.), 2:1:3-, m.p. 252—253° (decomp.), 2:1:4-, m.p. 256—257° (decomp.), and 2:1:5- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$, m.p. 247—248° (decomp.); *o*-, m.p. 164° (decomp.), and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 239° (decomp.); *o*-, m.p. 182—183°, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, m.p. 201—202°; *o*-, m.p. 223° (decomp.), and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, m.p. 211—212°; *o*-, m.p. 204—205° (decomp.), *m*-, m.p. 209°, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, m.p. 258° (decomp.); NHPh_2 , m.p. 206—207°; NHPhMe , m.p. 179—180°; $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, m.p. 181°; NH_2Ac , m.p. 237—238°; cyclohexylamine, m.p. 201°. M.p. are corr. A. T. P.

Azides as reagents for the identification of organic compounds. XVI. *m*-Nitrobenzazide as reagent for identification of phenols. P. P. T. SAH and T. F. WOO (Rec. trav. chim., 1939, 58, 1013—1017).—*m*-Nitrophenylurethanes of the following are prepared: PhOH , m.p. 125—126°; *o*-, m.p. 129—130°, *m*-, m.p. 109°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$, m.p. 141°; 1:2:4-, m.p. 130—131°, 1:4:5-, m.p. 129°, and 1:3:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$, m.p. 118—119°; α -, m.p. 144°, and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, m.p. 152—153°; *o*-, m.p. 116°, *m*-, m.p. 117—118°, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, m.p. 139°; *o*-, m.p. 135—136°, *m*-, m.p. 132—133°, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$, m.p. 139—140°; *o*-, m.p. 143°, *m*-, m.p. 164°, and *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{OH}$, m.p. 152—153°; 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{OH}$, m.p. 154°, and - $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{OH}$, m.p. 136°

(decomp.); 2:4:6:1- $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{OH}$, m.p. 169—170°, and - $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$, m.p. 201°; Me, m.p. 125°, Et, m.p. 217°, and benzyl salicylate, m.p. 117—118°; *o*-, m.p. 142—143°; *m*-, m.p. 97°, and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 131—132°; *o*-, m.p. 142—143°, *m*-, m.p. 163—164°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 197—198°; thymol, m.p. 113°; isothymol, m.p. 97°. M.p. are corr.

A. T. P.

Determination of constitutional groups of humic acids. II. R. R. GALLE and A. G. NIKOLAEV (J. Appl. Chem. Russ., 1939, 12, 923—933).—The material is hydrolysed, and the product treated with CH_2N_2 ; the sum of CO_2H and phenolic OH groups is then determined. A second portion of the hydrolysis product is methylated with Me_2SO_4 , and the sum of CO_2H , phenolic, and alcoholic OH groups is determined. R. T.

Photometric determination of tryptophan, tyrosine, di-iodotyrosine, and thyroxine. E. BRAND and B. KASSELL (J. Biol. Chem., 1939, 131, 489—501).—A photometric determination of tryptophan (I), tyrosine (II), di-iodotyrosine (III), and thyroxine (IV), based on the procedure developed by Lugg (A., 1937, III, 447; 1938, III, 546) from the Folin-Ciocalteu method (A., 1927, 892), is described. Standard vals. for the extinction coeffs. (Pulfrich refractometer) of (I) and (II) are given as well as correction factors for protein hydrolysates. (III) and (IV) give no Millon reaction before or after hydrolysis with alkali, but during hydrolysis with alkaline stannite both compounds yield reactive phenols. (III) and (IV) are determined indirectly from the total I and from the extra chromogenic material formed after hydrolysis with alkaline stannite. Representative results are given for cryst. egg-albumin, cattle fibrin, and several thyroid preps. The vals. for the (IV) content of thyroid preps. exceed those obtained by the method of Leland and Foster but are < those by the Harington method. The method has been applied to the determination of (IV) in technical thyroid preps. H. W.

Determination of uric acid.—See A., 1940, III, 84.

Identification of cocaine. New colour reaction. M. PESEZ (J. Pharm. Chim., 1939, [viii], 30, 200—206).—When cocaine (1—5 mg.) is added to H_2SO_4 (13—15 drops; *d* 1.84) containing conc. HNO_3 (2 drops) and heated at 100° for 5—10 min., cooled, and diluted with H_2O (1 c.c.), a yellow colour develops. If this liquid is shaken with COMe_2 and NaOH , the COMe_2 is coloured sky-blue, changing to violet and then red. Delcaine, alypine, and eucaine give similar reactions. The test applied to atropine, homatropine, hyoscyamine, duboisine, and scopolamine gives a red-violet colour. C_6H_6 and *N*-phenylmethylethylmalonylcarbamide also give an intense blue colour. The literature is reviewed. J. L. D.

Microchemical identification of brucine and strychnine with alkali iodide and chlorate. Applications. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1937, 75, 5—9; Chem. Zentr., 1937, i, 3191).—KI and NaClO_3 give characteristic cryst. ppts. with strychnine and brucine in dil. AcOH .

A. J. E. W.

A., II.—Organic Chemistry

FEBRUARY, 1940.

Cracking of olefines, diolefines, and cyclic unsaturated hydrocarbons.—See A., 1940, I, 76.

Kinetics of slow oxidation of ethylene.—See A., 1940, I, 76.

Hydrogenation of Δ^2 -heptene and *n*-heptane under pressure. A. F. NIKOLAEV and P. V. PUTSCHKOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 345—346).—Considerable amounts of isoheptanes (A) are formed when *n*-C₇H₁₆ is heated with H₂-Mo₂S₃ at 400°/140 atm. or when Δ^2 -*n*-heptene is hydrogenated in presence of Mo₂S₃ at 400°/250 atm. (A) contain *tert.* C, since much of the derived NO₂-compounds is insol. in KOH. R. S. C.

Catalytic oxidation of straight-chain olefines with hydrogen peroxide. W. TREIBS (Brennstoff-Chem., 1939, 20, 358—360).—Oxidation of Δ^2 -octene, Δ^2 -decene, undecene, etc. by H₂O₂ in COMe₂ or MeOH at 25—35° gives $\alpha\beta$ -unsaturated alcohols, α -glycols, aldehydes, osones, and monocarboxylic acids. Some of these undergo further oxidation; the reactions involved are briefly discussed. A. B. M.

Production of alkyl chlorides from alkyl ethers.—See B., 1940, 21.

Macromolecular compounds. CCXXXI. Polyvinyl chlorides. H. STAUDINGER and J. SCHNEIDERS (Annalen, 1939, 541, 151—195).—The prep., fractionation, methods of analysis, and chemical behaviour of polyvinyl chlorides are described. Data relating to osmotic pressure, f.p., and viscosity measurements are recorded and discussed. An account is given of chlorinated polyvinyl chlorides, oxygenated degradation products, and mixed polymerisates of vinyl chloride and vinyl acetate. F. L. U.

Mechanism of hydrolysis of $\alpha\gamma$ -dimethylallyl chloride.—See A., 1940, I, 30.

Action of hydrogen chloride on dimethyl- and methylethyl-bromoethinylcarbinol. A. I. ZACHAROVA (J. Gen. Chem. Russ., 1938, 8, 1224—1229).—OH·CMe₂·C·CBr and HCl in presence of CuCl and NH₄Cl (8 hr. at room temp.) afford γ -chloro- α -bromo- γ -methyl- Δ^2 -butinene, b.p. 48°/22 mm., and $\alpha\gamma$ -dichloro- α -bromo- γ -methyl- Δ^2 -butene, b.p. 72—74°/22 mm. OH·CMeEt·C·CBr and HCl similarly yield γ -chloro- α -bromo- γ -methyl- Δ^2 -pentinene, b.p. 65—66°/18 mm. R. T.

Aliphatic chloro-derivatives. XIV. Additive power of ethylenic linkings at quaternary carbon atoms. D. V. TISCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 1232—1246).—Certain previously

published work (cf. A., 1939, II, 530) has been revised; the reaction between CHMe·CMe₂ (I) and Cl₂ in presence of NaHCO₃ is now shown to involve the following reactions: (10—15%) CHMeCl·CMe₂Cl \leftarrow (I) \rightarrow CH₂·CMe·CHMeCl (II) (70—80%); (30%) CH₂Cl·CMeCl·CHMeCl \leftarrow (II) \rightarrow CH₂·C(CH₂Cl)·CHMeCl (III) (65%); (6%) CMeCl·C(CH₂Cl)₂ \leftarrow (III) \rightarrow CHMeCl·C(Cl)(CH₂Cl)₂ (90%). A no. of other ethylenic compounds reacted as follows: (CMe₂)₂ \rightarrow CH₂Cl·CMe·CMe₂ (90%); (60%) CHMe·CET·CET₂Cl \leftarrow (CET₂)₂ \rightarrow (CET₂Cl)₂ (40%); (68%) CH₂·CMe·CHCl₂ \leftarrow CHCl·CMe₂ \rightarrow CH₂Cl·CMe₂Cl (32%); (10%) CMe₂Cl·CMeCl₂ \leftarrow CMe₂·CMeCl \rightarrow CH₂·CMe·CMeCl₂ (80%); (45%) CHMeCl·CMeCl₂ \leftarrow CHMe·CMeCl \rightarrow CH₂·C(Cl)·CHMeCl (55%); CH₂Cl·C(Cl)·CHMe \rightarrow CH₂Cl·C(Cl)₂·CHMeCl (100%). It is concluded that an anomalous Lvov reaction may be expected in the case of compounds with a quaternary C atom under certain definite conditions of polarisation of the ethylenic linking, depending on the nature of the substituents. Elimination of HCl in the Lvov reaction takes place under conditions of steric hindrance of approach of Cl to the positive centre of the org. ion by the substituents of the quaternary C atom, as a result of which Cl' reacts with a H atom of one of these substituents. The following appear to be new: δ -chloro- $\delta\gamma$ -diethyl- Δ^2 -hexene, b.p. 70—72°/10 mm., $\gamma\gamma$ -dichloro- β -methyl- Δ^2 -propylene, b.p. 108—112°, isomerising at the b.p. to $\alpha\gamma$ -dichloro- β -methyl- Δ^2 -propylene, b.p. 131—131·5°, $\gamma\gamma$ -dichloro- β -methyl- Δ^2 -butylene, b.p. 124—126°, isomerising at the b.p. to $\alpha\gamma$ -dichloro- β -methyl- Δ^2 -butylene, b.p. 151—153°, γ -chloro- β -chloromethyl- Δ^2 -butylene, b.p. 39—40°/7 mm., $\alpha\beta\gamma$ -trichloro- β -methylbutane, b.p. 65—65·5°/11 mm. R. T.

Purification and criteria of purity of organic physico-chemical standards. L. GILLO (Ann. Chim., 1939, [xi], 12, 281—347).—The methods of purification and the possibility of preservation in a state of purity, and the degree of purity attainable, have been studied for MeOH, C₆H₆, and CHCl₃. In addition to chemical tests the methods used for determination of impurities included differential ebulliometry and the determination of the velocity of crystallisation. The most important impurities in MeOH are COMe₂ and H₂O. COMe₂ is not easily eliminated by distillation and must be chemically removed. After one distillation over Na, [H₂O] is ~0·003%, after a second distillation reduced to >0·0005%. The product contained <10⁻⁴% of COMe₂ and CH₂O, and is easily maintained in a state of purity if adequate precautions are taken against contamination with H₂O from the atm. or from the walls of glass vessels. CHCl₃, washed with H₂O and

twice distilled from P_2O_5 , contains $\sim 3 \times 10^{-4}\%$ of $COCl_2$ and HCl which cannot be diminished by further treatment and increases on keeping in presence of even a little air, although in complete absence of air the increase in impurity is only slight. Highly purified specimens (treated successively with H_2SO_4 , H_2O , Na_2CO_3 , and P_2O_5 , and then fractionated in an atm. of dry H_2) sometimes decompose spontaneously, liberating $COCl_2$. In the course of the decomp. the presence of a substance containing active O can be detected: it is less volatile than $CHCl_3$ and may be a peroxide, CO_2Cl_2 . C_6H_6 is easily dehydrated by distillation. A technical specimen free from C_4H_4S , after distillation, freezing out, and redistillation, contained $<0.001\%$ of H_2O . F. J. G.

Preparation of α -di-iodoisopropyl alcohol. G. LUSIGNANI (Boll. Chim. farm., 1939, 78, 557—558).—The prep. of $OH \cdot CH(CH_2I)_2$ is improved. $OH \cdot CH(CH_2Cl)_2$, from glycerol and HCl - $AcOH$ at 100 — 110° , is heated with NaI at 130 — 140° (bath), with stirring, under reflux. E. W. W.

Synthesis of acetylene γ -glycols. A. BABAJAN, B. AKOPJAN, and R. GIULI-KEVCHJAN (J. Gen. Chem. Russ., 1939, 9, 1631—1632).— C_2H_2 is passed into Et_2O - $COMe_2$ mixture containing KOH , at 9 — 10° (1—3 hr.). H_2O is added, with cooling, after 24 hr., and the Et_2O layer is separated and distilled; the residue consists chiefly of $(OH \cdot CMe_2 \cdot C)_2$. $COMeEt$ similarly affords $(OH \cdot CMeEt \cdot C)_2$, and cyclohexanone gives di-(1-hydroxycyclohexyl)acetylene. R. T.

Methods and apparatus used at the Bureau of Physicochemical Standards. XI. Purification and criteria of purity of organic standards. L. GILLO (Bull. Soc. chim. Belg., 1939, 48, 341—443).—The history, reactions, stability, methods of purification, and characterisation of Et_2O , $EtOH$, $EtOAc$, and CS_2 are given. W. R. A.

Syntheses of polyvinyl acetal.—See B., 1940, 19.

Decomposition of alkyl peroxides.—See A., 1940, I, 76.

Male hormone. XI. Activator of the male hormone. A. OGATA and I. KAWAKAMI (J. Pharm. Soc. Japan, 1939, 59, 126—127).—Trimethylene glycol monopalmitate, m.p. 42.0 — 43.5° , is derived from Ag palmitate and trimethylene bromohydrin at 100° . $COMe \cdot CH_2Cl$ and Na palmitate at 130 — 150° yield acetol palmitate, m.p. 50.5° (oxime, m.p. 55.5 — 56°). The activating power of ethylene glycol dipalmitate on male sex hormone greatly exceeds that of the monopalmitate. H. W.

Alkyl- and amyl-substituted silicic acid esters. IV. Hydrolysis and anhydridisation of alkyltriethoxysilanes. K. A. ANDRIANOV (J. Gen. Chem. Russ., 1938, 8, 1255—1263).—Hydrolysis of $SiR(OEt)_3$ ($R = Et, Bu^s$) results in production of $OH \cdot SiR(OEt)_2$, followed by its condensation, with elimination of H_2O , to yield products of the type $SiR(OEt)_2 \cdot [O \cdot SiR(OEt)_2]_x \cdot O \cdot SiR(OEt)_2$. The no. A of Si atoms in such products is given by $A = n/(n - m)$, where n is the concn. of $SiR(OEt)_3$, and m is the $[H_2O]$ of the reaction mixture. R. T.

Production of aliphatic anhydrides.—See B., 1940, 21.

Action of bromine on sodium ethoxide. L. N. PARENT'EEV and M. M. ABRAMOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 761—762).— $NaOEt$ and Br in dry Et_2O at 0° , then at 100° (bath), give a 58% yield of $EtOAc$. A. T. P.

Kinetics of thermal decomposition of ethyl formate.—See A., 1940, I, 28.

Esterase activity of benzoylcarbinol. C. LENTI (Arch. Sci. biol., Napoli, 1939, 25, 254—260).—Contrary to Langenbeek (A., 1936, 69, 514), benzoylcarbinol does not catalyse the hydrolysis of methyl butyrate (at 20° and 50°). S. O.

Long-chain acids. I. Extension of the isoprene rule. P. C. MITTER and P. N. BAGCHI (J. Indian Chem. Soc., 1939, 16, 402—404).—The isoprene rule is extended to explain the formation of some 12- and 16-C acids occurring in nature. Formation of mono- and di-basic long-chain aliphatic acids can be explained by assuming addition of H_2O at a conjugated double linking at one end of the chain, partial or complete hydrogenation and removal of the side-chain Me by oxidation, and partial or complete oxidation of the terminal groups; e.g., the relation of farnesol to sabinic acid is discussed. A. T. P.

Derivatives of ketonic aliphatic acids. A. GODFRIN (J. Pharm. Chim., 1939, [viii], 30, 321—326).— $CHAcR \cdot CO_2Et$ ($R = Me, Et, Pr^a$, or Pr^b) in H_2SO_4 at -5° to -10° with an equimol. amount of $NO \cdot HSO_4$ affords $CR(N \cdot OH) \cdot CO_2Et$, which with aq. $NH_2 \cdot CO \cdot NH \cdot NH_2 \cdot HCl$ or $NH_2 \cdot CS \cdot NH \cdot NH_2 \cdot HCl$ give the semicarbazones (I) and thiosemicarbazones (II) of the corresponding substituted pyruvic acids. The following are prepared: *Et β -methyl-*, m.p. 105° , *-ethyl-*, m.p. 99° , *-propyl-*, m.p. 118° , and *-isopropylpyruvate thiosemicarbazone*, m.p. 150° . (I) with dil. $NaOH$ at $100^\circ/3$ hr. (or at room temp./48 hr.) gives sulphonyl triazines (III) which yield Cu derivatives. The following are prepared: *5-keto-3-thiol-6-ethyl-*, m.p. 165° , *-propyl-*, m.p. 149° , *-butyl-*, m.p. 143° , and *-isobutyl-1:2:4-triazine*, m.p. 182° . (II) are not cyclised under similar conditions. When (III) are oxidised with $NaOBr$, the corresponding dihydroxytriazines are formed. The following are prepared: *3:5-dihydroxy-6-ethyl-*, m.p. 152° , *-butyl-*, m.p. 135° , and *-isobutyl-1:2:4-triazine*, m.p. 185° . J. L. D.

Action of periodic acid on pyruvic, acetic, and propionic acid. P. FLEURY and R. BOISSON (J. Pharm. Chim., 1939, [viii], 30, 307—316; cf. A., 1939, II, 532).— $0.1N \cdot AcCO_2H$ (I) (1 c.c.) is completely oxidised with the utilisation of 1 O by $0.1N \cdot HIO_4$ (5 c.c.) at 100° in 0.5 hr. Oxidation proceeds more slowly as the amount of (I) is increased, or at a lower temp. CO_2 formed is determined after aspiration into $0.2N \cdot NaOH$, and $AcOH$ by titration of the reaction mixture free from CO_2 , or of its steam-distillate. $AcOH$ is identified by steam-distilling the reaction mixture and converting the product into its Ca salt, which when heated gives $COMe_2$. $0.1N \cdot HIO_4$ (5 c.c.), $0.1N \cdot AcOH$ (2 c.c.), and H_2O (3 c.c.) when heated at 100° in a sealed tube do not react. $EtCO_2H$ is similarly unaffected. J. L. D.

Colour reaction of maleic anhydride, *p*-benzoquinone, and their partly-substituted derivatives. A. SCHÖNBERG and A. F. A. ISMAIL (Nature, 1939, 144, 910).—At room temp., a trace of maleic anhydride (I) gives an orange-red colour with a solution of PPh_3 in CHCl_3 or C_6H_6 . Mono- but not di-substituted derivatives of (I) react similarly. *p*-Benzoquinone and derivatives in which some, but not all, of the H are substituted also give the colour. Anthraquinone, phenanthraquinone, 2:3-dichloronaphthaquinone, and 2:6-dimethylpyrone give no coloration. L. S. T.

Electrolysis of the salts of dibasic organic acids (succinic, glutaric, pyrotartaric, and ethylmalonic acids) with nitrates. F. FICHTER and E. BLOCH (Helv. Chim. Acta, 1939, 22, 1529—1540).—Electrolysis of mixtures of KNO_3 and K_2 succinate yields $(\text{CH}_2\cdot\text{NO}_2)_2$ and $(\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2)_2$, but no alkyl nitrates. Similarly the three isomeric salts $\text{C}_3\text{H}_6(\text{CO}_2\text{K})_2$ yield glycol dinitrates but no alkyl nitrates when electrolysed with KNO_3 . It is inferred that C_2H_4 derivatives are not the intermediate products in the formation of alkyl nitrates by electrolysis of mixtures of the K salts of fatty acids with KNO_3 , but that these are formed by interaction of alcohols and HNO_3 at the anode. J. W. S.

Isomerisation of ethyl citrate to ketipate. S. N. NAUMOV and L. S. DEDUSENKO (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 24, 4 pp.).— Et_3 citrate yields $(\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ when treated with NaOEt in EtOH or Et_2O ; the reaction does not proceed in presence of Na alone. R. T.

Colorimetric determination of vitamin-C.—See A., 1940, III, 53.

Structure of alginic acid. I. E. L. HIRST, J. K. N. JONES, and (Miss) W. O. JONES (J.C.S., 1939, 1880—1885).—A detailed account of work already reported (A., 1939, II, 405). The following data are new. Trimethylmannuronide Me ester, b.p. (bath) $147^\circ/0.002$ mm., $[\alpha]_D^{20} +60.0^\circ$ in H_2O ; trimethylmannuronic acid, a syrup, $[\alpha]_D^{20} +36.4^\circ$ in H_2O ; 2:3-dimethylmethyl-d-mannuronide Me ester, b.p. (bath) $180^\circ/0.005$ mm., $[\alpha]_D^{20} +59^\circ$ in H_2O ; 2:3-dimethyl-d-mannuronic acid, a syrup, $[\alpha]_D^{20} +30^\circ$ in MeOH , $+33^\circ$ (const.) in 2% $\text{HCl}\cdot\text{MeOH}$, and -d-mannosaccharic acid, a syrup, $[\alpha]_D^{20} +16^\circ$ in H_2O , -7.5° in alkali. R. S. C.

Manufacture of hydroxy-aldehydes and -ketones.—See B., 1940, 22.

Reaction of keten with alcohols. I. P. TZUKER-VANIK and I. A. JERMOLENKO (Bull. Univ. Asiæ Centr. 1937, No. 22, 215—220).—Keten reacts rapidly and quantitatively with *p*-anisidine and with primary and sec. alcohols, and more slowly with *tert.* alcohols. With glycerol addition of a catalyst (H_2SO_4) is necessary. Keten does not react with the C=C group. R. T.

Catalytic preparation of acetone by dehydrogenation of isopropyl alcohol.—See B., 1940, 19.

Reaction of sodamide with non-enolising carbonylic compounds. L. C. FREIDLIN and A. I. LEBEDEVVA (J. Gen. Chem. Russ., 1939, 9, 1589—

1597).—Ketones react in the vapour phase with NaNH_2 , as follows: $\text{CORR}' + 2\text{NaNH}_2 \rightarrow \text{RH} + \text{R'H} + \text{NaHCN}_2 + \text{NaOH}$ ($\text{R} = \text{R}' = \text{Bu}^\vee$; $\text{R} = \text{Ph}$, $\text{R}' = \text{CPh}_3$; $\text{R} = \text{R}' = p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$). Fenchone reacts similarly, to give 1-methyl-3-isopropylcyclopentane. The following reactions are described: (at 215°) $\text{Me}_2\text{C}_2\text{O}_4 + 6\text{NaNH}_2 \rightarrow 2\text{NaHCN}_2 + 2\text{NaOH} + \text{H}_2 + 2\text{NaOMe} + 2\text{NH}_3$; (at 140°) $\text{CO}(\text{NH}_2)_2 + 2\text{NaNH}_2 \rightarrow \text{NaHCN}_2 + \text{NaOH} + 2\text{NH}_3$; (at 235°) $\text{CO}(\text{NHPh})_2 + 2\text{NaNH}_2 \rightarrow \text{NaHCN}_2 + \text{NaOH} + 2\text{NH}_2\text{Ph}$; (at 156°) $\text{Fe}(\text{CO})_5 + 10\text{NaNH}_2 \rightarrow 5\text{NaHCN}_2 + 5\text{NaOH} + 5\text{H}_2 + \text{Fe}$. R. T.

Thermal decomposition of diacetyl.—See A., 1940, I, 77.

Identification and determination of hexoses in polysaccharides and glycoproteins by the carbazole method.—See A., 1940, III, 84.

Oxidation of glucosone (2-ketoglucose) by hypiodite.—See A., 1940, I, 77.

3:4-Dimethylgalactose. J. S. D. BACON and D. J. BELL (J.C.S., 1939, 1869—1871).—3:4-isopropylidene- β -methylgalactoside and pure N_2O_5 in CHCl_3 give the 2:6-dinitrate, m.p. 79° , $[\alpha]_D^{25} +40.0^\circ$ in CHCl_3 (and some β -methylgalactoside 2:3:4:6-tetranitrate, m.p. $114\text{--}115^\circ$, $[\alpha]_D^{25} -12.4^\circ$ in CHCl_3 , $[\alpha]_D^{25} -7.1^\circ$ in EtOH , also obtained from β -methylgalactoside), which with $\text{N}\cdot\text{HCl}$ (5 ml.) in boiling COMe_2 (110 ml.) gives β -methylgalactoside 2:6-dinitrate, m.p. $110\text{--}111^\circ$, $[\alpha]_D^{25} +15.2^\circ$ in EtOH . MeI and a little COMe_2 at 45° then give (repeated treatment) 3:4-dimethyl- β -methylgalactoside 2:6-dinitrate (I), m.p. $75\text{--}76^\circ$, $[\alpha]_D^{25} -13.3^\circ$ in CHCl_3 , but in one experiment a Me_1 ether dinitrate, m.p. $114\text{--}115^\circ$, was obtained. With boiling $\sim 10\%$ $\text{NaOH}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$, (I) yields 3:4-dimethyl- β -methylgalactoside, m.p. $102\text{--}103^\circ$, $[\alpha]_D^{20} -9.1^\circ$ in CHCl_3 , hydrolysed by boiling $\text{N}\cdot\text{HCl}$ to 3:4-dimethyl- β -galactose (II), m.p. $164\text{--}166^\circ$, $[\alpha]_D^{20} +95^\circ \rightarrow +116.5\text{--}117.1^\circ$ in H_2O in 16—20 hr. The structure of (II) is proved by its mutarotation, method of formation, conversion into 2:3:4:6-tetramethylgalactoseanilide, and oxidation (Br) to 3:4-dimethylgalactono- δ -lactone, $[\alpha]_D^{25} +89.0^\circ \rightarrow +7.0^\circ$ in H_2O in 5240 min., and thence into the amide, m.p. $172\text{--}174^\circ$, which gives the Weerman test. R. S. C.

Agar-agar. II. Isolation of derivatives of 3:6-anhydro-l-galactose from agar. Synthesis of their enantiomorphs. I. A. FORBES and E. G. V. PERCIVAL (J.C.S., 1939, 1844—1849; cf. A., 1937, II, 445).—Mainly a detailed account of work already reported (A., 1939, II, 142; cf. *ibid.*, 99). The Me laevulate obtained from methylated agar by 6% H_2SO_4 originates in the anhydrogalactosides and is not evidence of ketoses. The anhydro-ring probably exists as such in agar. The Selivanov reaction is not sp. for ketoses. The following data appear new. β -Methyl-d-galactoside 6-p-toluenesulphonate triacetate, a glass, $[\alpha]_D^{20} -3^\circ$ in CHCl_3 ; 3:6-anhydro- β -methyl-d-galactoside, $[\alpha]_D^{20} -114^\circ$ in H_2O ; 2:4-dimethyl-3:6-anhydro-d-galactoseanilide, m.p. 118° , $[\alpha]_D^{20} +100^\circ \rightarrow +56^\circ$ in 1 day in EtOH ; Me 2:4-dimethyl-3:6-anhydro-d- and -l-galactonate, m.p. $49\text{--}50^\circ$, $48\text{--}49^\circ$, $[\alpha]_D^{25} +63^\circ$, -64° in H_2O , $+73^\circ$, -72.5° in CHCl_3 ,

respectively; 2:4-dimethyl-3:6-anhydro-d- and -l-galactonamide, m.p. 150°, 151°, $[\alpha]_D^{20} +75^\circ$, -74° in H_2O , respectively. R. S. C.

2:3:4-Trimethylmannose. W. N. HAWORTH, E. L. HIRST, F. ISHERWOOD, and J. K. N. JONES (J.C.S., 1939, 1878—1880).—The TI derivative of α -methyl-d-mannoside 6-CPH₃ ether (cf. Watters *et al.*, A., 1939, II, 407), m.p. 100°, $[\alpha]_D^{20} +20^\circ$ in $CHCl_3$, and boiling MeI give 6-triphenylmethyl-2:3:4-trimethyl- α -methyl-d-mannoside, m.p. (crude) 106—110°, $[\alpha]_D^{20} +33^\circ$ in $CHCl_3$, hydrolysed by addition of H_2O to its solution in boiling AcOH to 2:3:4-trimethyl- α -methyl-d-mannoside, b.p. (bath) 150°/0.005 mm., $[\alpha]_D^{20} +38^\circ$ in $N-HCl$. 2N-HCl at 90° then gives 2:3:4-trimethyl-d-mannose (I), $[\alpha]_D^{20} +2^\circ$ in H_2O , oxidised by Br to 2:3:4-trimethyl-d-mannolactone, $+H_2O$, m.p. 73°, $[\alpha]_D^{20} +138^\circ \rightarrow +81^\circ$ in H_2O in 95 hr. [readily gives the amide, m.p. 143°, $[\alpha]_D^{20} +5^\circ$ in H_2O (negative Weerman test)], and by HNO_3 (*d* 1.42) to 2:3:4-trimethyl-d-mannosaccharic acid [diamide (II), m.p. 228° (decomp.), $[\alpha]_D^{20} -17^\circ$ in MeOH, -14° in H_2O (positive Weerman test)]. (I) and (II) differ from the substances previously so named (Haworth *et al.*, A., 1935, 477; 1937, II, 277). R. S. C.

β -Methylfructofuranoside. H. H. SCHLUBACH and H. E. BARTELS (Annalen, 1939, 541, 76—85).— β -Methylfructofuranoside (I), $[\alpha]_D -49.95^\circ$, $[\alpha]_{5461} -58.92^\circ$ in H_2O , prepared essentially by Morgan's method (A., 1927, 749; 1928, 1214), undergoes almost quant. hydrolysis by invertase (II). Contrary to Morgan, α - and β -methylfructosidediphosphoric acids (Ba salts, $[\alpha]_D +8.5^\circ$ and -8.75° , respectively) are dephosphorylated by kidney-phosphatase and are practically unaffected by (II). Hydrolysis ($N-H_2SO_4$) of (I) (half-period 52.5 min.) occurs less readily than for the α -isomeride (half-period 34 min.). H. B.

Emulsin. XL. Glucosides of isethionic acid and its ethyl ester. B. HELFERICH and H. LUTZ-MANN (Annalen, 1939, 541, 1—16).—*Ag isethionate*, m.p. 110° (from the acid and Ag_2CO_3), and acetobromoglucose in C_6H_6 at 50°, followed by Ag_2CO_3 at room temp. in the dark, give a $COMe_2$ -sol. Ag salt converted by EtI into *Et tetra-acetyl- β -d-glucosidoisethionate* (I), m.p. 125°, $[\alpha]_D^{10} -15.4^\circ$ in $CHCl_3$, hydrolysed (Zemplen) to *Et β -d-glucosidoisethionate* (II), m.p. 89°, $[\alpha]_D^{21} -24.1^\circ$ in H_2O . β -d- β -Chloroethylglucoside (III), m.p. 67—68° (slight previous sintering), $[\alpha]_D^{10} -29.2^\circ$ in H_2O , is obtained from its tetra-acetate (IV), new m.p. 119—120° (improved prep.; cf. Coles *et al.*, A., 1938, II, 261). β -d- β -Bromoethylglucoside (V), m.p. 74—75° (slight previous sintering), $[\alpha]_D^{10} -26.1^\circ$ in H_2O , and its tetra-acetate, m.p. 118°, $[\alpha]_D^{20} -12.3^\circ$ in $CHCl_3$, are described. β -d- β -Iodoethylglucoside (VI), m.p. 120—121°, $[\alpha]_D^{18} -25.3^\circ$ in H_2O [tetra-acetate, m.p. 100—101°, $[\alpha]_D^{20} -11.9^\circ$ in $CHCl_3$, from (IV) and $COMe_2-NaI$ at 100° (sealed tube)], with aq. Na_2SO_3 (1 mol.) at 60° gives *Na β -d-glucosidoisethionate* ($+H_2O$) (VII), m.p. (anhyd.) 130—131° (slight previous sintering), $[\alpha]_D^{18} -32.9^\circ$ in H_2O , which on successive acetylation ($AcOH-Ac_2O-C_5H_5N$), acidification ($COMe_2-MeOH$ -conc. H_2SO_4), and esterification ($CHMeN_2$) affords (I). Aq. solutions of (II) undergo hydrolysis (slow at room temp.; rapid at 100°) to the free acid, $[\alpha]_D^{18} -34.4^\circ$ in

H_2O (not isolable), which is remarkably stable to acids and does not reduce Fehling's solution. The glucoside linking in (II) is very sensitive to alkali; 0.01N-NaOH (0.2 mol.) at $\sim 20^\circ/5$ hr. and 0.05N-NaOH (1 mol.) at $\sim 19^\circ/7$ hr. cause fission of 47 and 100%, respectively, of glucose. The above β -d-glucosido-compounds are all hydrolysed by emulsin; the rates are (VI) > (V) > (III) > (II) \gg (VII). M.p. are corr. H. B.

Composition of the polysaccharide of firmly bound lipins of leprosy bacillus.—See A., 1940, III, 170.

Pectic substances. IV. Citrus araban. G. H. BEAVEN, E. L. HIRST, and J. K. N. JONES (J.C.S., 1939, 1865—1868; cf. A., 1939, II, 203).—Purified commercial citrus pectin contains Me pectate ~ 78 , araban (I) $\sim 7\%$, galactan, and smaller amounts of other substances, including hesperidin. (I), isolated by boiling with 70% EtOH and purified by pptn. from EtOH by $COMe_2$ and finally by acetylation, is identical with that from other sources (*loc. cit.*), differences in $[\alpha]$ being due to impurities. It is similarly hydrolysed and is converted by the action of MeI on the TI derivative at 45° into a Me derivative, which with boiling 2% HCl-MeOH gives an equimol. mixture of 2:3:5-trimethyl-l-arabofuranose, 2:3-dimethyl- and 3-methyl-l-arabinose (identified by $[\alpha]$ and conversion into the lactones and amides). All the arabinose units are furanose and probably have the α -configuration. All pectins consist essentially of pectic acid, usually as Me ester, with araban, galactan, and other materials. (I) cannot be derived from pectic acid by decarboxylation of galacturonic residues. R. S. C.

Polysaccharides. XXXVIII. Constitution of glycogen from fish liver and fish muscle. W. N. HAWORTH, E. L. HIRST, and F. SMITH (J.C.S., 1939, 1914—1922).—Glycogens obtained from fish liver (dogfish, haddock, and hake) and muscle (dogfish) give acetates and thence Me ethers, end-group assay of which shows in all cases 12 glucose residues for each repeating unit. The amount of dimethylmethylglucoside isolated may depend partly on the degree of methylation, but is never < that of the Me_4 ether. The repeating units are thus joined by primary valencies from a reducing end of a chain to an OH not on C_{11} or C_{41} to form macro-mols. which from their non-reducing character and osmotic pressure contain 3000—5000 residues per mol. All the glycogens except that from haddock liver were insol. in H_2O , but became sol. therein when dissolved in AcOH or mineral acid and pptd. by EtOH; reversion (during 4 months) to the insol. form is inexplicable. R. S. C.

Polysaccharides. XXXIII. Methylation of cellulose in air and in nitrogen. W. N. HAWORTH, E. L. HIRST, L. N. OWEN, S. PEAT, and (in part) F. J. AVERILL. XXXIV. Methylation of cellulose in an inert atmosphere. W. N. HAWORTH, R. E. MONTANA, and S. PEAT (J.C.S., 1939, 1885—1898, 1899—1901; cf. A., 1939, II, 495).—XXXIII. $COMe_2$ -insol. cellulose triacetate (prep. from cotton linters described) swells in dioxan or dioxan- $COMe_2$ to a viscous solution, which is readily methylated at

55°. This and the COMe_2 -sol. acetate (Ac 30%), cotton slivers and linters are methylated by Me_2SO_4 -NaOH in air and N_2 at varying temp. (15–60°) for a varying no. of treatments. Each product is used for determination of the no. of glucose units per mol. by a modified end-group assay, osmotic pressure in CHCl_3 , and by η in CHCl_3 and, sometimes, *m*-cresol. This no. varies widely; results by osmotic pressure are < those by end-group assay.

XXXIV. Methylation of cotton slivers is heterogeneous and not reproducible. After 30 treatments 7% was insol. in CHCl_3 and thus contained <40% of OMe. Methylation involves progressive diminution of particle size, tending to a min. of ~200 glucose units after 25–30 treatments. A sample methylated 15 times had as average 450 glucose units per mol. as determined osmotically, but <700 as determined by end-group assay. R. S. C.

Polysaccharides. XXXV. Hydrocellulose. H. C. CARRINGTON, W. N. HAWORTH, E. L. HIRST, and M. STACEY. **XXXVI. Hydrocellulose.** W. N. HAWORTH, S. PEAT, and W. J. WILSON (J.C.S., 1939, 1901–1904, 1904–1908).—XXXV. Hydrocellulose (I), a friable powder of which 30% is sol. in aq. NaOH, is converted into mixed acetates and thence into mixed Me derivatives (OMe 45%). The no. of glucose units per mol. is then 70 by end-group assay, 95 by I no., or 54 by η in *m*-cresol. (I) is probably a product of simple hydrolytic degradation of cellulose.

XXXVI. Fibrous hydrocellulose (Cu no. 2-6) is separated mechanically into fibre (Cu no. 1-7) and powder (Cu no. 5-4), gives only glucose (91% from the fibre, 92% from the powder) when hydrolysed, contains no enolic OH, CO_2H (CH_2N_2), or uronic acid groups, and with Me_2SO_4 -30% aq. NaOH-dioxan gives mixed ethers, the main fraction (70%; OMe 45-5%) of which is shown by end-group assay to contain (average) 120 glucose units per mol. The fibre gives a main ether fraction (60%), containing 200 (by end-group assay) or 70 (by I no.) units per mol. The fibre and powder give Ac derivatives (Ac 43–44-5%), containing, according to η in *m*-cresol, 98 and 65 (73 by I no.) units per mol., respectively. The relative solubilities in 0-25 and 2-5N-NaOH are cellulose < fibre < powder hydrocellulose < dextrin (18 units) < dextrin (12 units). Hydrocelluloses vary mainly or only in chain-length, with which the solubility in alkali varies inversely. R. S. C.

Polysaccharides. XXXVII. Oxy-cellulose. G. L. GOODMAN, W. N. HAWORTH, and S. PEAT (J.C.S., 1939, 1908–1914).—Fibrous oxy-cellulose (I) prepared by means of 0-25N- KMnO_4 has Cu no. 14, contains uronic acid residues (~1-5% CO_2 by direct and conductometric titration, determination of furfuraldehyde and of CO_2 liberated by boiling acid), and is only slowly acetylated to a product (Ac 43-7%), $[\alpha]_D^{20}$ -21° in CHCl_3 , containing 60–70 glucose units per mol. (η in *m*-cresol). Extraction with 0-25N-NaOH gives approx. equal parts of sol. (II) and insol. material (III). (III) has Cu no. 0-27, contains no uronic acid groups, gives readily a heterogeneous acetate and a Me derivative, separable by fractional pptn. into portions having (end-group assay) 110, 92,

and 55 glucose units per mol., the main fraction (60%) having 90 units per mol. During these assays excellent yields of 2:3:6-tri- and tetra-methylglucose are obtained. Thus, (III) resembles hydrocellulose in nature and the peculiarities of (I) are due to the (II). Isolation of (II) is impracticable, as dissolution in NaOH [3% $\text{Ba}(\text{OH})_2$ in air or N_2 gives similar results] causes decomp. to HCO_2H (5%), AcOH, and acids identified by methylation as *d*-lactic acid (characterised as *d*-OMe·CHMe·CO·NH₂), $\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{CO}_2\text{H}$, and $\text{C}_5\text{H}_7(\text{OH})_4\cdot\text{CO}_2\text{H}$ [gives a lactone ether, $\text{C}_6\text{H}_7\text{O}_2(\text{OMe})_2$, $[\alpha]_D^{20} +64\cdot4^\circ$ (and thence an acid, $[\alpha]_D -7\cdot5^\circ \rightarrow +32\cdot4^\circ$ in 25 hr.), and an ester, $\text{C}_5\text{H}_7(\text{OMe})_4\cdot\text{CO}_2\text{Me}$ (derived acid, $[\alpha]_D -4\cdot8^\circ$)]. De-comp. of (II) by acid thus resembles that of a mono-saccharide. The uronic acid groups of (II) are decomposed also by acid, cold 72% H_2SO_4 giving an aldobionic acid (*Ba* salt, $[\alpha]_D +61\cdot7^\circ$) and subsequent boiling with 1% H_2SO_4 giving 81% of (glucose + α -methylglucoside) [90% in all isolated similarly from (III)]. Approx. half the (III) is dissolved by cold 2-5N-NaOH, but decomp. is general as the sol. fraction (which is homogeneous) has 35 (end-group assay) or 33 (η) and the insol. 60 (by η of the acetate in *m*-cresol) units per mol. Formation of oxy-cellulose thus involves oxidation of some $\text{CH}_2\cdot\text{OH}$ to CO_2H and much fragmentation of the chain to give alkalinsol. oligosaccharides (max. chain-length 30–35 units) of high reducing power. R. S. C.

Synthesis of choline esters. Dimorphism of higher analogues. M. LOURY (Compt. rend., 1939, 209, 682–684).—Choline esters are obtained with the base hydrochloride by interaction of $\text{R}\cdot\text{COCl}$ with $\text{NMe}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ (2 mols.) in dry Et_2O at 0° or as their hydrochlorides (which are subsequently treated with $\text{KOH}\cdot\text{EtOH}$ or Ag_2O) when 1 mol. of base is used. β -Dimethylaminoethyl palmitate, b.p. 187°/3 mm., laurate, b.p. 155°/3 mm., and stearate, b.p. 205°/3 mm., m.p. 25°, are described. Some of the compounds are obtained in dimorphic forms.

J. L. D.

Amino-acids. I. Partition of acetamido-acids between immiscible solvents. II. Separation of amino-acids by means of their *N*-acetyl derivatives. III. Isolation of hydroxyamino-acids from protein hydrolysates. IV. Methyl ethers of some *N*-acetyl-hydroxyamino-acids. R. L. M. SYNGE (Biochem. J., 1939, 33, 1913–1917, 1918–1923, 1924–1930, 1931–1934).—I. A list of the partition coeffs. of some NH_2 -acids between CHCl_3 and H_2O , EtOAc , and H_2O , and showing the effect of temp. on the coeff. of acetyl-*d*-leucine between H_2O and CHCl_3 , is given. The following have been prepared: acetyl-dl- α -aminobutyric acid, m.p. 129–131°; -1-hydroxyproline; -d(-)-isoleucine, m.p. 150–151°, $[\alpha]_D^{25} -11\cdot5^\circ$ in H_2O ; -d(+)-leucine, m.p. 186–188°, $[\alpha]_D^{25} +23\cdot2$ in EtOH ; -d-norleucine, m.p. 112–114°, $[\alpha]_D^{25} -0\cdot2^\circ$ in EtOH ; *N*-acetyl-dl-serine; acetyl-l-valine, m.p. 157–158°, $[\alpha]_D^{20} +5\cdot8^\circ$ in EtOH .

II. A complex mixture of NH_2 -acids is acetylated by Ac_2O and NaOH at 0°. After neutralisation with H_2SO_4 the conc. mixture is extracted with CHCl_3 , the aq. phase is evaporated, the residue extracted with EtOH , and the NH_2 -acid mixture re-acetylated.

This is repeated a third time and three CHCl_3 -sol. fractions are obtained. Extract I contains neither arginine nor serine.

III. The prep. of *N*-acetyl-*O*-benzoyl-*dl*-serine, m.p. 192—194°, and *l*-hydroxyproline, m.p. 185—186°, $[\alpha]_D^{20}$ -42.9° in EtOH, is described. These compounds can be debenzoylated by 0.1*N*-NaOH at room temp., and deacetylated by boiling *N*- H_2SO_4 . These properties form the basis of a method of isolation of a hydroxy-amino-acid fraction from hydrolysates of fibrin, wool, and gelatin.

IV. The prep. of the following *N*-acetyl-*O*-methyl-hydroxyamino-acids is described and the partition coeffs. between CHCl_3 and H_2O are given: *l*-tyrosine *Me* ester, m.p. 106—107°, $[\alpha]_D^{20}$ +26.3° in EtOH; *l*-tyrosine, m.p. 150—151°, $[\alpha]_{5461}^{20}$ +67.6° in EtOH; *l*-hydroxyproline *Me* ester, m.p. 76—77°, $[\alpha]_D^{20}$ -81.0° in EtOH; *l*-hydroxyproline, m.p. 152—153°, $[\alpha]_D^{20}$ -104.3° in EtOH; *dl*-serine *Me* ester, m.p. 70—71°; *dl*-serine, m.p. 108—109°; *dl*-allothreonine, m.p. 151°. The properties of these derivatives might be made the basis of a fractionation of hydroxyamino-acids in protein hydrolysates. P. G. M.

Methionine. IV. Colour reaction of methionine. J. J. KOLB and G. TOENNIES (J. Biol. Chem., 1939, 131, 401—407).—Methionine (I) and CuCl_2 in conc. HCl give a mol. compound [(I) + HCl + CuCl_2] the colour of which closely resembles that of I-KI solutions, varying from dark brown to pale yellow according to concn. Reaction is not observed with cysteine, cystine, homocysteine thiolactone, or methionine sulphoxide. A definite but weak colour is obtained with *S*-methylcysteine. *S*-Benzyl- and *S*-methyl-cysteine give a faint colour whereas the reaction of djenkolic acid is almost and that of *S*-carboxymethyl- and *S*-phenyl-cysteine entirely negative: Bu_2S , $\text{CS}(\text{NH}_2)_2$, methyl- and benzyl-isothiocarbamide, thioacetanilide, thiophen, Ph_2S , $(\text{CH}_2\text{Ph})_2\text{S}$, and thiamine are inactive whereas homomethionine, hexomethionine, ethionine, and homodjenkolic acid are as active as (I). The faintly positive action of $\text{SEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ shows that the NH_2 -acid structure is not essential for the reaction. The available evidence suggests that the reaction is one of org. sulphide S, the adjoining groups of which satisfy certain conditions. All compounds which give the reaction in full intensity have the group $[\text{CH}_2]_2\cdot\text{S}\cdot\text{CH}_2\cdot$ in common but the chromogenic val. of this structure is not independent of the nature of the attached groups. Solubility in H_2O is also essential. (I) is the only natural NH_2 -acid which gives a definite response to the HCl- CuCl_2 reaction. This is not inhibited by carbohydrates (glucose, sucrose, starch) or alkaloids (brucine, cinchonidine, or quinine) but various proteins give a distinct, positive response. The sensitivity of the test is relatively low owing to unavoidable interference with the colour by the reagent itself. Qual. observations are best made by slowly bringing particles of the solid in contact with the reagent. The chlorides of Fe, Co, or Ni do not show an analogous activity and solutions of CuCl_2 in conc. H_2SO_4 , H_3PO_4 , or AcOH produce no colour with (I). H. W.

1939, II, 404).— CrCl_3 and NH_4MeCl in CS_2 with NaOMe or NaOEt give *Cr* tris-*N*-methyl-, no m.p., and -ethyl-dithiocarbamate. *Cr* tris-*N*-isobutyl-, m.p. 220—222° (decomp.), and -NN-diethyl-dithiocarbamate, m.p. ~250° (decomp.), are obtained from the corresponding Na dithiocarbamate, and *Cr* tris-NN-di-n-butyl-dithiocarbamate, m.p. 119—120°, from CrCl_3 and NH_4Bu_2 in CS_2 . Aq. $\text{NR}_2\cdot\text{CS}_2\text{Na}$ (I) and Na_2MoO_4 (II) slowly acidified with HCl give molybdenyl bis-NN-dimethyl-, -diethyl- (III), and -di-n-butyl-dithiocarbamate. $\text{C}_5\text{H}_5\text{N}$ and (III), or (I), (II), and SO_2 or (best) $\text{Na}_2\text{S}_2\text{O}_4$ give the salt $(\text{Net}_2\cdot\text{CS}_2)_4\text{Mo}_2\text{O}_3$, which with acids gives the salts $(\text{Net}_2\cdot\text{CS}_2)_4\text{Mo}_2\text{O}_3(\text{XOH})_2$ (X = CHO, Ac, or EtCO), and on long boiling the product, $(\text{Net}_2\cdot\text{CS}_2)_2\text{Mo}_2\text{O}_3(\text{OH})_2$ ($3\text{C}_5\text{H}_5\text{N}$ compound, slowly converted into a $\text{C}_5\text{H}_5\text{N}$ compound). $\text{UO}_2(\text{NO}_3)_2$ and $\text{Net}_2\cdot\text{CS}_2\text{Na}$ etc. give uranyl bis-NN-diethyl-dithiocarbamate, and corresponding bis-NN-*Pr*^a₂, and -*Bu*^a₂, and bis-*N*-*Et* and -*Bu*^b compounds. Similar derivatives of W are not obtained. E. W. W.

Mechanism of urea formation.—See A., 1940, III, 40.

β-Alkylthiosemicarbazides. E. CATTELAINE (Compt. rend., 1939, 209, 799—801).—Alkylhydrazines and KCNS give the corresponding thiocyanates which are isomerised at 140—165° to β-alkylthiosemicarbazides. The following are described: thiocyanates of mono-methyl- and -benzylhydrazine (oils); β-methyl-, m.p. 183—184°, and -benzyl-thiosemicarbazide, m.p. 155°; benzaldehyde β-methyl-, m.p. 174°, and -benzyl-, m.p. 215.5°, anisaldehyde β-methyl-, m.p. 192°, and -benzyl-, m.p. 175°, and p-methoxyhydratropaldehyde β-methyl-, m.p. 100°, and -benzyl-thiosemicarbazone, m.p. 195°.

J. L. D.

Racemisation of optically active co-ordination compounds. Application of Arrhenius equation.—See A., 1940, I, 77.

Co-ordinated copper compounds with propylenediamine. P. NEOGI and K. L. MANDOL (J. Indian Chem. Soc., 1939, 16, 433—436).— $\text{C}_3\text{H}_6(\text{NH}_2)_2$ with Cu^{++} salts gives bispropylenediamine-cupric bromide, iodide, sulphate, nitrate, tartrate, sulphonate, and chloride; the last is converted by Ag_2O into the hydroxide and this by nitrocamphor into the nitronate.

F. R. G.

Metallo-organic tin derivatives. S. N. NAUMOV and Z. M. MANUILKIN (Acta Univ. Asiae Mediae, 1937, [vi], No. 31, 12 pp.).— SnCl_4 and MgMeI in Et_2O are heated at the b.p. for 5 hr., the Et_2O is distilled off, and the residue is heated at 120—140° for 8 hr., to yield SnMe_4 . This with I in Et_2O gives SnMe_3I , which with MgEtI gives SnMe_2Et . A succession of such reactions affords SnMeEtPrI , attempts at resolution of which into optical antipodes were unsuccessful. R. T.

Co-ordination compounds of αγ-diaminoisopropanol. J. G. BRECKENBRIDGE and J. W. R. HODGINS (Canad. J. Res., 1939, 17, B, 331—335).—When $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{NH}_2)_2$ (= dap) co-ordinates with Co^{++} salts it gives, by spontaneous oxidation, derivatives $\text{Co}(\text{dap})_2^+$ of Co^{+++} identical with those prepared directly from the Co^{+++} salts (Mann, A., 1928,

Dithiocarbamates of metals of group VI. L. MALATESTA (Gazzetta, 1939, 69, 752—762; cf. A.,

157). On drying over P_2O_5 at 100° the products from both sources lose $2H_2O$ to give $Co[OH \cdot C(CH_2 \cdot NH_2)_2]_3$ in which the $OH \cdot C(CH_2 \cdot NH_2)_2$ is a tridentate group. The crystals are monoclinic with $a:b:c = 1.134:1:0.861$, $\beta = 110^\circ 27'$, and combine the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $q\{\bar{1}11\}$. Some of the crystals are twinned on $a\{100\}$. Cu^{++} gives crystals $CuX_2(dap)_2$ [$X = Cl$, decomp. 181° ; $= Br$; $= NO_3$, decomp. 160° after softening at 0.5°], which do not lose water at 100° with P_2O_5 . $AgNO_3$ forms unstable white needles of $Ag(dap)NO_3 \cdot 0.5H_2O$ and $ZnCl_2$ a microcryst. product $ZnCl_2 \cdot C_3H_5ON_2$, the empirical formula of which changes on recrystallisation. T. H. G.

trans-cis Isomerisation of cobaltic complexes.—See A., 1940, I, 30.

Complexes formed by molybdic acid in aqueous solution.—See A., 1940, I, 80.

Kinetics of cracking of hydrocarbons under pressure. II, III.—See A., 1940, I, 29.

Polymerisation of cyclopentadiene and α -dicyclopentadiene. Explosive decomposition of cyclopentadiene.—See A., 1940, I, 29.

Hydrogenation of cyclohexene with copper catalysts.—See A., 1940, I, 33.

Physical properties and chemical constitution. IV. **Methylcyclohexane.** Multiplanar structure of the methylcyclohexane ring. D. M. COWAN, G. H. JEFFERY, and A. I. VOGEL (J.C.S., 1939, 1862—1865; cf. A., 1938, II, 436).—Methylcyclohexanes-A are impure *B'*-form, into which they pass when kept or distilled over Na. *B'* is stable when kept; its parachor is 281.4. $Zn-Hg-HCl-AcOH$ reduces 2- (I), 3- (II), b.p. $169^\circ/756$ mm., or 4-methylcyclohexanone (III) to mixtures (containing methylcyclohexenes), hydrogenation (PtO_2) of which gives only *B'*. Wolff-Kishner reduction of the semicarbazones of (I) and (III) gives the *B*-form, which passes when kept into *B'*, but the semicarbazone of (II) gives an unstable hydrocarbon, which may contain some of a third form. Although *B* is not always obtained by the methods given, it is considered to be a definite steric isomeride of *B'*. R. S. C.

Halogenation. XXI. Direct replacement of aromatic sulphonie groups by chlorine and bromine atoms. P. S. VARMA, N. B. PAREKH, and V. K. SUBRAMANIAM (J. Indian Chem. Soc., 1939, 16, 460—462).—About 50 sulphonie acids and their Na salts, when heated strongly over a naked flame with Cu_2Cl_2 or Cu_2Br_2 , yield the corresponding Cl- or Br-derivatives. F. R. G.

Kinetics of reaction of *m*-chloronitrobenzene with aqueous ammonia in presence of cupric chloride.—See A., 1940, I, 31.

Electrolytic nitration of aromatic hydrocarbons. I. Nitration of xylene in methyl alcohol. II. Nitration of benzene and toluene in methyl alcohol. III. Nitration of xylene, toluene, and benzene in aqueous medium. I. A. ATANASIU and C. BELCOT (Bull. Acad. Sci. Roumaine, 1937—8, 19, 28—36, 101—105, 106—108).—I. The electrolyte is a mixture of *m*-xylene (I) (30.6%), HNO_3 (d 1.48, 30.4%), C^* (A., II.)

and MeOH (39%). The nitration process of (I) consists in an electrolytic concn. of HNO_3 at the anode followed by a simple chemical action between HNO_3 and (I). Stirring inhibits the local accumulation of HNO_3 and hence the nitration process. The change is confined to the production of a $(NO_2)_1$ -derivative, which is the main product of the reaction; oxidation products insol. in H_2O and small amounts of oxidation products sol. in H_2O and EtOH are also formed. The best results are obtained by use of graphite electrodes and of a diaphragm which diminishes the amounts of by-products to a min. The most suitable temp. is $40-45^\circ$ with c.d. 0.1 amp. per sq. cm. for each 10 c.c. of electrolyte.

II. Under like conditions, the electrolytic nitration of PhMe is very similar to that of (I). The change proceeds only to the formation of $C_6H_4Me \cdot NO_2$, which is the main product. Oxidation causes the formation of substances sol. and insol. in H_2O and $H_2O-EtOH$ with picric acid (II); the amounts exceed those formed when (I) is used. Use of a porous diaphragm greatly increases the yield of $C_6H_4Me \cdot NO_2$ and greatly diminishes that of the oxidation products. C_6H_6 is nitrated to only a very small extent and the main change is an oxidation leading chiefly to insol. oxidised products with some sol. compounds and (II). Electrochemical nitration therefore depends on the chemical nature of the substrate as well as on the conditions of electrolysis.

III. Electrolysis of a well-stirred suspension of (I) in HNO_3 (d 1.2) with Pt on graphite electrodes preferably at 60° gives a $(NO_2)_1$ -derivative in much smaller yield than that obtained in a homogeneous medium (see above) so that the process has no practical significance. The yields of $C_6H_4Me \cdot NO_2$ are very small and only traces of $PhNO_2$ are produced. The quantities of oxidation products are very small in all cases. Without agitation and with the hydrocarbon forming a thin layer above the acid on the electrodes dipping into both liquids preferably at $40-50^\circ$ the yields of NO_2 -compound of (I), PhMe, or C_6H_6 are inferior to those obtained with stirring probably because there is only slight contact between hydrocarbon and acid which operates only in the immediate anodic layer. There is no evidence of the formation of $PhNO_2$. The amounts of oxidation products are very small. H. W.

Analysis of benzyl chloride.—See B., 1940, 19.

Isomerisation of allene hydrocarbons in presence of silicates. VII. **Phenylallene.** J. M. SLOBODIN (J. Gen. Chem. Russ., 1938, 8, 1220—1223).— $CHPh:CH \cdot CH_2 \cdot OH$ and HBr yield a bromohydrin, which when heated with KOH at $150-175^\circ/100$ mm. gives a mixture of $CHPh:C:CH_2$ (64%) and $CPh:CMe$ (36%). R. T.

Fission of tetra-arylmethanes by liquid alloys of potassium and sodium. P. P. SCHORIGIN and I. V. MATSCHINSKAJA (J. Gen. Chem. Russ., 1939, 9, 1546—1558).— $p-CHPh_2 \cdot C_6H_4 \cdot CPh_3$ (I) or CPh_4 does not decompose in boiling $EtOBz$ or decahydronaphthalene, nor do they react with Na in liquid NH_3 . With 5:1 K-Na in Et_2O at room temp. (I) decomposes, yielding benzyl- Δ^2 - or Δ^3 -cyclohexane (II), b.p. $140-141^\circ/38$ mm., and triphenylcyclohexenylmethane m.p.

168.5—169.5°. Under similar conditions: CPh_4 yields (II), CHPh_3 , CH_2Ph_2 , and C_6H_6 . Probable reaction schemes are presented.

R. T.

Catalytic transformations of the dimeride of $\Delta^{1:3}$ -cyclohexadiene. E. V. ALEXEEVSKI (J. Gen. Chem. Russ., 1939, 9, 1586—1588).—The dimeride is hydrogenated (Pt-black; 24 hr. at room temp.) to 1:4-endoethylenedecahydronaphthalene, b.p. 101.9°/7.5 mm. Dehydrogenation with Pd at 320—380° gives a product, $\text{C}_{12}\text{H}_{14}$, m.p. 62.5°, of undetermined structure. The dimeride when heated with floridin at 300—320° yields polymerides readily oxidised by atm. O_2 .

R. T.

Molecular dissymmetry due to symmetrically placed hydrogen and deuterium. The α -pentadeuterophenylbenzylamine problem. G. R. CLEMO and G. A. SWAN (J.C.S., 1939, 1960—1961).—Repetition of the work described (A., 1936, 977) on the resolution of α -pentadeuterophenylbenzylamine gives an inactive base (cf. Adams *et al.*, A., 1938, II, 271). The C_6D_6 now used had m.p. 5.5°.

J. D. R.

Optical rotatory powers of 4-substituted benzhydrylamines. G. R. CLEMO, C. GARDNER, and R. RAPER (J.C.S., 1939, 1958—1960).—Contrary to Cohen *et al.* (A., 1915, i, 661), 4-methylbenzhydrylamine (I) could not be resolved through its *d*-bromocamphorsulphonate, m.p. 228° (lit. 208°), $[\alpha]_D +57.5^\circ$. $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and (I) in $\text{EtOH}\cdot\text{K}_2\text{CO}_3$ yield Et *N*-4-methylbenzhydrylaminoacetate, b.p. 185—195°/1 mm., hydrolysed by $\text{EtOH}\cdot\text{KOH}$ to the acid, m.p. 185°, which when treated successively with SOCl_2 and NH_3 gives a substance, $\text{C}_{16}\text{H}_{15}\text{ON}$, m.p. 207°, probably 4-keto-1-*p*-tolyl-1:2:3:4-tetrahydroisoquinoline. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COPh}$ and $\text{HCO}\cdot\text{NH}_2$ at 170—180°/18 hr. yield form-4-bromobenzhydrylamide, m.p. 127—128°, hydrolysed ($\text{HCl}\cdot\text{EtOH}$) to *dl*-4-bromobenzhydrylamine, b.p. 155—160°/1 mm., $[\alpha]_D -7.1^\circ$, $[\alpha]_{5461} -12.8^\circ$, $[\alpha]_{4358} -24.6^\circ$ in EtOH (*Ac* derivative, m.p. 183°). The base recovered from the mother-liquors from the crystallisation of (II) yields with *l*-tartaric acid *d*-4-bromobenzhydrylamine *l*-tartrate, m.p. 205°, $[\alpha]_D -6.8^\circ$ in H_2O , from which the *d*-base, $[\alpha]_D +10.2^\circ$ in EtOH (*Ac* derivative, m.p. 183°), is recovered. By similar reactions is formed *dl*-4-chlorobenzhydrylamine, b.p. 146°/1 mm. (formyl, m.p. 124°, and *Ac* derivative, m.p. 130—131°), which is resolved via the *l*-base *d*-tartrate, m.p. 199°, $[\alpha]_D +9.8^\circ$ in H_2O , and *d*-base *l*-tartrate, m.p. 199°, $[\alpha]_D -9.86^\circ$ in H_2O , into *d*-, b.p. 146°/1 mm., $[\alpha]_D +10.8^\circ$ in EtOH (*Ac* derivative, m.p. 169°), and *l*-4-chlorobenzhydrylamine, b.p. 145—150°/1 mm., $[\alpha]_D -10.9^\circ$, $[\alpha]_{5790} -12.9^\circ$, $[\alpha]_{5461} -14.6^\circ$, $[\alpha]_{4358} -25.2^\circ$ in EtOH (*Ac* derivative, m.p. 169°). From $p\text{-C}_6\text{H}_4\text{I}\cdot\text{COPh}$ is formed *dl*-4-iodobenzhydrylamine, b.p. 173—176°/1 mm. (formyl, m.p. 143°, and *Ac* derivative, m.p. 170°), resolved via the *l*-base *d*-tartrate, m.p. 206°, $[\alpha]_D +3.58^\circ$ in H_2O , and *d*-base *l*-tartrate, m.p. 205°, $[\alpha]_D -3.8^\circ$ in H_2O , into *l*-, $[\alpha]_D -10.6^\circ$, $[\alpha]_{5790} -12.2^\circ$, $[\alpha]_{5461} -13.7^\circ$, $[\alpha]_{4358} -23.9^\circ$ in EtOH (*Ac* derivative,

m.p. 195—196°), and *d*-4-iodobenzhydrylamine, $[\alpha]_D +10.6^\circ$ in EtOH (*Ac* derivative, m.p. 195°).

J. D. R.

Auto-oxidation of aromatic amines.—See A., 1940, I, 35.

Rearrangement of *N*-chloroacetanilide in chlorobenzene solution.—See A., 1940, I, 32.

2:4:6-Trichloro-5-nitro-*m*-toluidine and derivatives. E. BUREŠ and A. SPITNIKOVÁ (Časop. Českoslov. Lék., 1937, 17, 189—195).—2:4:6-Trichloroacet-*m*-toluidine is easily nitrated to the 5- NO_2 -derivative, m.p. 207°, hydrolysed to 2:4:6-trichloro-5-nitro-*m*-toluidine (I), m.p. 171° (*Ac*, m.p. 141°, *Bz*, *N-Me*, m.p. 158°, and *N-Et*, m.p. 170°, derivatives). (I) is converted into 2:4:6-trichloro-3-nitrotoluene, m.p. 54° (also obtained by nitration of 1:2:4:6- $\text{C}_6\text{H}_2\text{MeCl}_3$) (reduced to the 3- NH_2 -derivative, m.p. 85°), and 2:4:6-trichloro-3-bromo-, m.p. 168°, and 3-iodo-5-nitrotoluene, m.p. 130°. Introduction of NO_2 into the 1:2:4:6:3- $\text{C}_6\text{HMeCl}_3\cdot\text{NH}_2$ mol. increases its stability and resistance to chemical agents.

F. R.

3:5-Dibromo- and 3:5:6-tribromo-*p*-xylydine and derivatives. E. BUREŠ and F. MEŠKAN (Časop. Českoslov. Lék., 1937, 17, 149—160).—Bromination of *p*-xylydine in EtOH out of sunlight gives 3:5-dibromo-*p*-2-xylydine, m.p. 67—68° (*Ac*, m.p. 56°, and *Bz*, m.p. 192°, derivatives), which is converted (diazo-methods) into 2:6-dibromo-, m.p. 36°, 2-chloro-3:5-dibromo-, m.p. 85°, and 2:3:5-tribromo-*p*-xylene, 3:5-dibromo-*p*-2-xylenol, m.p. 82° (*Me* ether, m.p. 39—40°; *Hg* and *Bi* salts), and 2:4-dibromo-3:6-dimethylbenzonitrile, m.p. 97°. 2-Acet-amido-*p*-xylene and Br in AcOH give the 3:5:6-*Br*₃-derivative, m.p. 256°, hydrolysed to 3:5:6-tribromo-*p*-2-xylydine, m.p. 195—197°, whence 2:3:6-tribromo-, m.p. 83°, 2-chloro-3:5:6-tribromo-, m.p. 179°, tetrabromo-, m.p. 106°, and 3:5:6-tribromo-2-iodo-*p*-xylene, m.p. 67°, and 3:5:6-tribromo-*p*-2-xylenol, m.p. 177°. Progressive bromination of *p*-xylydine increases the stability of the mol. F. R.

Hydrolysis of substituted benzenesulphonanilides. IV. Solubility of sulphonanilides in water and hydrochloric acid. R. L. SHRINER, J. D. OPPENLANDER, and R. S. SCHREIBER (J. Org. Chem., 1939, 4, 588—591; cf. A., 1934, 288, 996).—Study of the solubilities of benzene- and *p*-toluenesulphonanilide and their Me, Et, Pr^a, and Bu^a derivatives in H_2O and HCl of const. b.p. shows that the solubility of each series in either solvent decreases as the size of the alkyl group increases and that the ratio of the solubility in aq. HCl to that in H_2O is >1 and rises to a max. val. and then decreases. The increase in the solubility of $\text{ArSO}_2\cdot\text{NPhAlk}$ in aq. HCl may be one of the reasons why they are hydrolysed by acids more rapidly than $\text{ArSO}_2\cdot\text{NPh}$. Benzenesulphonmethylanilide has b.p. 187—189°/2 mm., m.p. 37—38°. Benzenesulphon-*n*-butylanilide, b.p. 182—184°/1 mm., m.p. 33°, is new. H. W.

Kinetics of the reaction of *p*-chloroaniline, 1-chloronaphthalene, and sodium 1-chloronaphthalene-4-sulphonate with aqueous am-

monia in presence of cuprous chloride.—See A., 1940, I, 31.

Mechanism of catalytic phenylation and its inhibition by iron.—See B., 1940, 19.

Nitrones. V. Action of potassium cyanide on carbamyl nitrones. VI. Synthesis of benzylidenecarbamides. V. BELLAVITA and (SIGNA.) N. CAGNOLI (Gazzetta, 1939, 69, 583—594, 602—608).—V. The appropriate ArCHO with KCNO, $\text{NH}_2\text{OH}\cdot\text{HCl}$, and H_2O give *N*-carbamyl-*p*-chloro-, decomp. 132—135°, *p*-dimethylamino-, decomp. 164—165°, and 4-hydroxy-3-ethoxy-benzylidene-, decomp. 139—140°, and *resorcyli*dene-nitrone, decomp. 132—135°. Nitrones of type $\text{CHR}\cdot\text{NO}\cdot\text{CO}\cdot\text{NH}_2$ with KCN in MeOH or EtOH give the following (m.p. of Ac and Bz derivatives indicated in parentheses): *benzylidene*.* (Bz, 103°), *cinnamylidene*.*, m.p. 75—77° (Bz, 123°), *cuminyli*dene.*, m.p. 110° (Bz, 125°) [from *N*-carbamylcuminyliidenenitrone, decomp. 143—145° (cf. Conduché, A., 1908, i, 154)], *o*.*, m.p. 103° (Ac, 111°; Ac₂, 70°; Bz, 123°), and *m*-nitrobenzylidene.*, m.p. 123·5° [Ac (Ac₂ ?), 131°; Bz, 175°], *p*-chlorobenzylidene.*, m.p. 112° (Ac, 73°; Bz, 147°), *salicyli*dene.*, b.p. 125°/25 mm. (Bz, 118°), *anisyli*dene.*, m.p. 66—67° (Ac, 51°; Bz, 110°), *p*-dimethylaminobenzylidene.*, m.p. 147° (Ac, 108°; Bz, 152°), *p*iperonyli)dene.*, m.p. 113·5° (Ac, 108—109°; Bz, 167°), 4-hydroxy-3-ethoxy-benzylidene.*, oily (ON-Bz₂, 141°), and *furfuryli*dene-carbamide.* m.p. 132—133° (Bz, 135°).

VI. KCNS, $\text{NH}_2\text{OH}\cdot\text{HCl}$, and ArCHO do not give arylidene-thiocarbamyl nitrones or -thiocarbamides, but -carbamides. The compounds marked * above are obtained in this way, as are *p*-nitrobenzylidene-, m.p. 131° (Ac, 128°; Bz, 196°), *resorcyli*dene-, m.p. 198° (Ac, 77°; Bz, 152°), and *vanillyli*dene-carbamide, m.p. 122° (Ac, 103—104°; Bz, 152°). E. W. W.

Raschig process for preparation of phenol.—See B., 1940, 19.

Iodination of halogenated phenols. P. S. VARMA and (MISS) K. M. YASHODA (J. Indian Chem. Soc., 1939, 16, 477—478).—Iodination (cf. Datta and Prosad, A., 1917, i, 332) by I-KI in aq. NH_3 of *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, 1:3:4- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{OH}$, and 1:5:2- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{OH}$ yields respectively 4:2:1- $\text{C}_6\text{H}_3\text{ClI}_2\cdot\text{OH}$ (acetate, m.p. 57°) or 4:2:6:1- $\text{C}_6\text{H}_2\text{ClI}_2\cdot\text{OH}$ (acetate, m.p. 128°), 3-bromo-5-iodo-*p*-cresol, m.p. 46° (benzoate, m.p. 115°), and 5-bromo-3-iodo-*o*-cresol, m.p. 49° (acetate, m.p. 40°; benzoate, m.p. 85°). F. R. G.

Iodination of organic compounds in presence of oxidising agents. T. D. ALDOSCHIN and V. S. TSCHALICHJAN (J. Gen. Chem. Russ., 1939, 9, 748—752).—From a study of the iodination of various phenols at 20° with KI + various oxidising agents it is concluded that the most suitable oxidising agents are chloramine-*T* and CaOCl_2 in acid, and CaOCl_2 in neutral, media. V. A. P.

Simple formation of *o*-nitrosophenol from benzene and hydroxylamine by atmospheric oxidation. Preparation of *o*-nitrosophenol and nitrosocresol from benzene and toluene by oxidation with hydrogen peroxide. O. BAUDISCH (Naturwiss., 1939, 27, 768—769).—When $\text{Cu}(\text{NO}_3)_2$

(0·66 g.) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (2 g.) in H_2O (200 c.c.) containing guanidine carbonate (I) (0·2 g.) (p_H thereby rises from 1·9 to 2·2) are shaken in air with C_6H_6 (20 c.c.), *o*-NO- $\text{C}_6\text{H}_4\cdot\text{OH}$ (II) is formed and isolated by extraction with light petroleum after acidification. (II) affords two red Cu derivatives, one insol., the other sol. in light petroleum. With $\text{Cu}(\text{OAc})_2$ [for $\text{Cu}(\text{NO}_3)_2$], no (I) is necessary as the p_H is 3·78. Autoxidation proceeds at p_H 2·2—4; at >4, yellow and brown by-products are formed. PhMe is not similarly converted into a nitrosocresol (III). C_6H_6 and PhMe are converted by H_2O_2 in presence of aq. $\text{Cu}(\text{NO}_3)_2$ or $\text{Cu}(\text{OAc})_2$ and $\text{NH}_2\text{OH}\cdot\text{HCl}$ into (II) and (III), respectively. J. L. D.

Simple formation of nitrosophenols from phenols. O. BAUDISCH and S. H. SMITH (Naturwiss., 1939, 27, 769).—PhOH (1 g.), $\text{Cu}(\text{OAc})_2$ or $\text{Cu}(\text{NO}_3)_2$ (2 g.), and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0·7 g.) in H_2O (100 c.c.) with perhydrol (2 c.c.) for several days at 0° afford a complex salt of *o*-NO- $\text{C}_6\text{H}_4\cdot\text{OH}$ which is isolated (15—20% yield) after acidifying. $\text{Ni}(\text{OAc})_2$ or $\text{Ni}(\text{NO}_3)_2$ gives only small yields. *p*-Cresol similarly yields nitroso-*p*-cresol, m.p. 58·5—59°; *o*- and *m*-cresol yield similar coloured complexes. J. L. D.

Action of carbon monoxide-hydrogen mixtures on cresol under pressure. W. KRÖNIG (Brennstoff-Chem., 1939, 20, 355—356).—When *m*-cresol is passed with CO + H_2 over a MeOH-forming catalyst, e.g., $\text{ZnO}\cdot\text{Mn}_2\text{O}_3$, at 500°/200 atm. part is reduced to the corresponding hydrocarbon but a large proportion is methylated to (probably) $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$. A. B. M.

Action of nitrous acid on certain halogenated substitution products of 2:5-, 3:4-, and 3:5-dimethylphenol. L. C. RAIFORD and D. W. KAISER (J. Org. Chem., 1939, 4, 555—568).—2:5:3:4:6:1- $\text{C}_6\text{H}_2\text{Me}_2\text{Br}_3\cdot\text{OH}$ is converted by NaNO_2 in AcOH-dioxan at 7—10° into 3:6-dibromo-4-nitro-2:5-dimethylphenol, m.p. 152—153° (decomp.) (*Me ether*, m.p. 85—86°; acetate, m.p. 114—115°), which is oxidised (fuming HNO_3 at 0°—room temp.) to 3:6-dibromo-*p*-xyloquinone, m.p. 185—186°, and reduced by SnCl_2 and HCl to 3:6-dibromo-4-amino-2:5-dimethylphenol, m.p. 187—188° (decomp.) [*hydrochloride*, decomp. ~225°; ON-Ac₂, m.p. 237—238°; N-Ac, m.p. 230—231° (decomp.), ON-Bz₂, m.p. >275°; N-Bz, m.p. 221—222°, N-benzoyl-O-acetyl, m.p. 244—245°, and O-benzoyl-N-acetyl, m.p. 250—251°, derivatives]. Rapid addition of conc. HNO_3 in AcOH to 3:4:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ in AcOH cooled by tap H_2O gives 8% of the $(\text{NO}_2)_2$ -derivative, m.p. 126—127°, and 38% of 6:3:4:1-NO₂- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$. The latter compound is converted by Br in AcOH containing Fe powder at 100°, by Br in CS_2 containing AlBr_3 at room temp., or by Br without solvent into 2-bromo-6-nitro-3:4-dimethylphenol, m.p. 74—75°. This is reduced by SnCl_2 and HCl to 2-bromo-6-amino-3:4-dimethylphenol, m.p. 103—104° (*hydrochloride*, decomp. ~260°; ON-Ac₂ derivative, m.p. 199—200°), into which a second Br could not be introduced. 3:4:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ is transformed by Br into 3:4:2:5:6:1- $\text{C}_6\text{H}_2\text{Me}_2\text{Br}_3\cdot\text{OH}$, m.p. 173—174°, converted by NaNO_2 and AcOH into 2:5-dibromo-6-nitro-3:4-dimethyl-

phenol, m.p. 168—169° (decomp.) (*Me ether*, m.p. 100—101°). This is reduced by SnCl_2 and HCl to 2 : 5-dibromo-6-amino-3 : 4-dimethylphenol, decomp. 130—131° (hydrochloride, decomp. ~230°; *ON-Ac*, m.p. 217—218°, *N-Ac*, m.p. 181—182°, *ON-Bz*, m.p. 207—208°, *N-Bz*, m.p. 227—228°, *N-benzoyl-O-acetyl*, m.p. 209—210°, derivatives). 2 : 3 : 5 : 1- $\text{NO}_2\text{-C}_6\text{H}_2\text{Me}_2\text{-OH}$ and Br in AcOH at 100° afford 4 : 6-dibromo-2-nitro-3 : 5-dimethylphenol, decomp. 160—161° (*Me ether*, m.p. 99—100°), which is reduced to 4 : 6-dibromo-2-amino-3 : 5-dimethylphenol, m.p. 141—142° [hydrochloride, decomp. ~241°; *ON-Ac*, m.p. 244—245° (decomp.), *N-Ac*, m.p. 190—191°, *ON-Bz*, m.p. 178—179°, *N-Bz*, m.p. 224—225° (decomp.), and *N-benzoyl-O-acetyl*, m.p. 175—176°, derivatives]. Chlorination of 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Me}_2\text{-OH}$ in hot CCl_4 gives 3 : 5 : 2 : 4 : 6 : 1- $\text{C}_6\text{H}_3\text{Me}_2\text{Cl}_3\text{-OH}$ (I), m.p. 177—178°, in 87% yield, oxidised by fuming HNO_3 to 2 : 6-dichloro-*m*-xyloquinone, m.p. 177—178°. This is reduced by NH_2OH in aq. EtOH at 100° to 2 : 6-dichloro-*m*-xyloquinhydrone, m.p. 177—178°, or by a larger proportion of NH_2OH (better by SnCl_2) to 2 : 6-dichloro-*m*-xyloquinol, m.p. 225—226°. Gradual addition of NaNO_2 to (I) in glacial AcOH at room temp. gives the mol. compound, $\text{C}_{24}\text{H}_{20}\text{O}_4\text{Cl}_2$, orange crystals which become yellow at 118—119° and melt slowly to a yellow liquid at 133—164°. Further evidence has been obtained to support the view that, in general, only one benzoyl-acetyl derivative can be prepared from an *o*- NH_2 -phenol regardless of the order of introduction of the acyl radicals.

H. W.

Structure of the dimeric forms of *o*-isopropenylphenols. W. BAKER and D. M. BESLY (*Nature*, 1939, 144, 865).—The properties of these compounds can be explained satisfactorily if they are regarded as derivatives of flavan.

L. S. T.

Steric hindered halogen addition by triaryl phosphites. L. ANSCHÜTZ, H. KRAFT, and K. SCHMIDT (*Annalen*, 1939, 542, 14—28).—*Tri- α -naphthyl*, m.p. 91°, and *tri- β -naphthyl phosphite*, m.p. 94°, afford the respective dichlorides and dibromides, which are hydrolysed to the corresponding phosphates, but *tri*-(2 : 4-dibromo-1-naphthyl), m.p. ~289° (darkening), and *tri*-(1 : 6-dibromo-2-naphthyl) phosphite (I), m.p. ~245° (darkening), do not. The failure to add halogen is ascribed to the size of the aromatic group (rather than the electronegative character of the *o*-Br) since *tri*-9-anthranyl phosphite (II), decomp. 182—190°, does not give a dihalide (some nuclear substitution occurs). The dichloride of (I) exists and is obtained (crude) from 1 : 6 : 2- $\text{C}_{10}\text{H}_5\text{Br}_2\text{-OH}$ and PCl_5 at 140—150° in CO_2 ; it is hydrolysed (boiling H_2O) to *tri*-(1 : 6-dibromo-2-naphthyl) phosphate, m.p. 200—201° (decomp.). The dichloride of (II) is similarly produced from anthrone (Barnett *et al.*, *J.C.S.*, 1923, 123, 2006) or anthranol and is hydrolysed to *tri*-9-anthranyl phosphate (III). 1- $\text{C}_{10}\text{H}_7\text{-MgBr}$ and PCl_3 give *tri- α -naphthylphosphine* (IV), m.p. ~282° (compounds with 1CHCl_3 , m.p. 262°, and 0.5CCl_4); its dibromide and dichloride [isolable only as compounds with 1CHCl_3 , m.p. 160° (decomp.), or 0.5CCl_4] are hydrolysed (dil. NaOH) to the hydrate of ($\alpha\text{-C}_{10}\text{H}_7$) $_3\text{PO}$ (V). *Tri*-9-anthranylphosphine could not

be prepared from Mg 9-anthranyl bromide and PCl_3 or from anthracene, PCl_3 , and AlCl_3 in CS_2 . The above phosphites (prep. from the appropriate phenol and PCl_3), (III), (IV), and (V) show fluorescence in ultra-violet light.

H. B.

Alkylation of phenol and anisole by the Friedel-Crafts reaction. I. P. TZUKERVANIK and N. D. TAMBOVTZEVA (*Bull. Univ. Asiatic Centr.*, 1937, No. 22, 221—225).— PhOMe , *iso*- $\text{C}_5\text{H}_{11}\text{Cl}$, and AlCl_3 in ligroin (4 hr. at 100°) yield *isoamyl*, b.p. 120—122°/11 mm., and *diisoamyl-anisole*, b.p. 137—140°/11 mm.; *isobutylanisole*, b.p. 126—127°/16 mm., is obtained similarly with Bu^βCl . With PhOH the reactions are: $\text{PhOH} + \text{AlCl}_3 \rightarrow \text{AlCl}_2\text{-OPH} (+\text{RCl}) \rightarrow \text{PhOR} (+\text{RCl}) \rightarrow \text{C}_6\text{H}_4\text{R-OR} (+\text{HCl}) \rightarrow \text{C}_6\text{H}_4\text{R-OH}$ ($\text{R} = \text{Bu}^\alpha, \text{CH}_2\text{Bu}^\beta$). The following were thus prepared: *p*-butylphenol, b.p. 129—130°/11 mm., butylphenyl *Bu ether*, b.p. 144—147°/11 mm. With *iso*- $\text{C}_5\text{H}_{11}\text{Cl}$ a mixture of *iso*- and *tert*-amyl derivatives was obtained.

R. T.

Sulphonates of higher alkyl phenolic ethers. G. S. HARTLEY (*J.C.S.*, 1939, 1828—1834).—Improved preps. of the following ethers are given; *Ph cetyl* (I), m.p. 42°, *p*- (II), m.p. 42.5°, *m*- (III), m.p. 35°, and *o*-tolyl cetyl (IV), m.p. 21.5°, *o*- (V) (an oil) and *p*-tolyl dodecyl (VI), m.p. 23.5°, pyrocatechol (VII), m.p. 23.5°, resorcinol (VIII), m.p. 37.5°, and quinol dioctyl (IX), m.p. 56°, resorcinol dihexyl (X), m.p. 12.5°, dioctyl (XI), m.p. 37.5°, hexyl octyl (XII), m.p. 15°, hexyl decyl (XIII), m.p. 27°, *Bu* dodecyl (XIV), m.p. 29.5°, *Et* tetradecyl (XV), m.p. 30.5°, octyl decyl (XVI), m.p. 31°, hexyl dodecyl (XVII), m.p. 34°, *Bu* tetradecyl (XVIII), m.p. 34°, *Et* hexadecyl (XIX), m.p. 37.5°, didodecyl (XX), m.p. 60°, and dihexadecyl (XXI), m.p. 71.5°. Sulphonation of ethers with a free *p*-position (where reaction probably occurs) is carried out with conc. H_2SO_4 at 70°, and of ethers with no free *p*-position (probable *o*-substitution) with ClSO_3H in CHCl_3 . Free sulphonic acids from (I)—(IV) and disulphonic acids from (VIII) (hexahydrate) and (XVII) (dihydrate) are obtained. The *K* salts of monosulphonates of (I)—(IX), (XIII)—(XIX), and of resorcinol octyl dodecyl and *Bu* hexadecyl ethers, and of the disulphonates of (XI), (XVII), (XX), and (XXI) are described, and methods of purification of the sulphonic acids and their salts, all of which are surface-active, are detailed.

J. D. R.

Hydrolysis or alcoholysis of resorcinol ether sulphonic acids. G. S. HARTLEY (*J.C.S.*, 1939, 1834—1836).—The mono- and di-sulphonic acids of *m*- $\text{C}_6\text{H}_4(\text{O-C}_8\text{H}_{17-n})_2$ (I) are rapidly hydrolysed by EtOH , $\text{Pr}^\alpha\text{OH}$, and $\text{OH}[\text{CH}_2]_2\text{OEt}$ (II) to (I); the rate of hydrolysis is reduced by H_2O in the solvent, but is little affected by mineral acid except when H_2O is present. Hydrolysis also occurs in dioxan and COMeEt , if 5% of H_2O is present. It is suggested that the SO_3H group is undissociated and can then react with any OH group. 6% of *Ph cetyl ether* is obtained from its 4-sulphonic acid and (II)- HCl ; ether hydrolysis also occurs.

J. D. R.

Synthesis of myristicin. V. M. TRIKOUJUS and D. E. WHITE (*Nature*, 1939, 144, 1016).—Allylation of pyrogallol 1-*Me ether* gives a good yield of two

liquid monoallyl ethers [(I) and (II); 3:5-dinitrobenzoates, m.p. 111—112°, and 134°, respectively]. Pyrolysis of (I), probably the 1-Me 2-allyl ether, gives 4:5-dihydroxy-3-methoxy-1-allylbenzene, which with CH_2I_2 + anhyd. K_2CO_3 in COMe_2 gives myristicin, b.p. 95—97°/0.2 mm. (30% yield) [Br_2 -derivative dibromide (III), m.p. 127—128°], whence isomyristicin, m.p. 43.5° (Br_2 -derivative dibromide, m.p. 158.5°). Pyrolysis of (II) gives a mixture which, on methylenation and bromination, yields mainly (III).

L. S. T.

Synthesis of 5:2':4'-trimethoxy-3:6:3'-trimethyldiphenyl ether. S. SHIBATA (J. Pharm. Soc. Japan, 1939, 59, 111—113).—1:2:6- $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2$ with Br in AcOH yields 3-bromo-2:6-dimethoxytoluene, b.p. 106—107°/5.5 mm., which with 3:2:5:1- $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{OK}$ (prep. in MeOH) and Cu at 180—230° gives 5:2':4'-trimethoxy-3:6:3'-trimethyldiphenyl ether, m.p. 110°, identical with the decarboxylation product of hypoparrellic acid Me_2 ether. J. D. R.

" $\alpha\alpha'$ -Dinaphthyl," a by-product in the preparation of perylene. B. N. LUNDIN (J. Gen. Chem. Russ., 1939, 9, 682—683).—The by-product m.p. 154°, obtained by Scharvin *et al.* (A., 1929, 1181) in the prep. of perylene and stated to be " $\alpha\alpha'$ -dinaphthyl," is now shown to be 1:1'-dinaphthylene 2:2'-oxide. V. A. P.

Preparation of diethylmetanilic acid and diethyl-*m*-aminophenol.—See B., 1940, 20.

Pinacolin rearrangement of 1:2-dimethylcyclohexane- and -cyclopentane-1:2-diols. H. MEERWEIN (Annalen, 1939, 542, 123—129).—Oxidation (KMnO_4 + MgSO_4 in aq. EtOH) of 1:2-dimethyl- Δ^1 -cyclohexene gives a mixture, b.p. 80—82°/1 mm., of *cis*-1:2-dimethylcyclohexane-1:2-diol (I), b.p. 102—103°/10 mm., m.p. 49.5—50°, and $\beta\eta$ -diketo-octane (II), m.p. 44°. (I) and (II) are not separable by distillation or (completely) by crystallisation; (II) is removed as its disemicarbazone, m.p. 222—222.5°. Dehydration of (II) with hot 20% H_2SO_4 affords 2-acetyl-1-methyl- Δ^1 -cyclopentene (III). Contrary to Bartlett *et al.* (A., 1937, II, 288), dehydration (2% H_2SO_4 at 150—160°) of (I) gives 1-acetyl-1-methylcyclopentane, b.p. 50.2—50.9°/11 mm. [oxidised (NaOBr) to 1-methylcyclopentane-1-carboxylic acid], and not 2:2-dimethylcyclohexanone [the compound described as this by Bartlett may be impure (III)]. Contrary to Bartlett *et al.* (A., 1938, II, 487), the difference in behaviour of *cis*- and *trans*-1:2-dimethylcyclopentane-1:2-diol is one of degree rather than kind; 2:2-dimethylcyclopentane-1:2-diol is obtained in 7 and 22% yield from the *trans*-diol with boiling 30% H_2SO_4 and conc. H_2SO_4 (at -10°), respectively. 1:2-Epoxy-1:2-dimethylcyclopentane has b.p. 120—122°/atm. pressure (Bartlett gives 120—122°/20 mm.). H. B.

Iodoso-compounds as oxidation agents. R. CRIGEE and H. BEUCKER (Annalen, 1939, 541, 218—238).—The velocity of the reaction between anethole (I) and aryl iododiacetates, $\text{ArI}(\text{OAc})_2$ (A), in AcOH at 20° falls in the order $\text{Ar} = p$ -tolyl, *m*-4-xylyl, *m*-tolyl, *o*-tolyl, Ph, m - $\text{NO}_2\cdot\text{C}_6\text{H}_4$, *p*- $\text{PhSO}_2\cdot\text{C}_6\text{H}_4$, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$; the bimol. coeffs. gradually decrease with time in all cases and are all of the same order [as is

that for $\text{Pb}(\text{OAc})_4$]. $\text{CHCl}_3\text{:CHI}(\text{OAc})_2$ resembles (A; $\text{Ar} = \text{Ph}$ or *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$). cyclopentadiene with (A; $\text{Ar} = \text{Ph}$, *m*-4-xylyl, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$) in AcOH at 30° gives 52—73% of diacetoxy-cyclopentenes; the cyclopentandiacetates obtained by subsequent hydrolysis ($\text{N}\cdot\text{KOH}$) and reduction (H_2 , Pt-black, EtOH) are shown [by oxidative fission of the 1:2-isomeride (II) (43—60%) present] to contain 40—57% of (*cis* + *trans*)-1:3-diol (III), b.p. 85—93°/1 mm. (*bis*-phenylcarbamates, m.p. 143° and 173°). The production of (III) shows preliminary 1:4 addition of 2 OAc to the conjugated system; such addition also occurs with $\text{Pb}(\text{OAc})_4$ in AcOH (43%) and C_6H_6 (19% of total product) (cf. A., 1930, 1278). (II) consists of *cis*- (41—59%) and *trans*-forms (59—41%). Fission of $\alpha\beta$ -glycols by $\text{PhI}(\text{OAc})_2$ occurs much more slowly than with $\text{Pb}(\text{OAc})_4$ (A., 1933, 1272); reaction is bimol. and the velocity coeffs. at 20° (k_{20}) are: *cis*- (115) and *trans*- (1.21) -7:8-dihydroxy-7:8-diphenylacenaphthene; isohydrobenzoin (IV) (0.28); *cis*- (0.073) and *trans*- (0.0084) -9:10-hydroxy-9:10-diphenyl-9:10-dihydrophenanthrene; *cis*-decahydronaphthalene-9:10-diol (0.0004); *cis*- (0.0008) and *trans*- (very small) -cyclohexane-1:2-diol. Reaction probably proceeds through a cyclic intermediate, $\begin{smallmatrix} >\text{C}\cdot\text{O} \\ >\text{C}\cdot\text{O} \end{smallmatrix} > \text{IPh}$. With (IV) and various (A),

the varying rates are (with few exceptions) in the reverse order for (I) (above). There is no simple relationship between velocity of oxidation of (IV) by $\text{PhI}(\text{O}\cdot\text{COR})_2$ in C_6H_6 and the strength of RCO_2H ($\text{R} = \text{Me}$, CH_2Cl , CHCl_2 , CCl_3) (k_{20} 2.0, 9.4, 10.4, and 8.3, respectively). $\text{H}_2\text{C}_2\text{O}_4$ is oxidised by (A) in AcOH; the possible relationship between ease of oxidation and the basic character of (A) in AcOH is discussed. In some respects, *e.g.*, non-formation of inorg. products, (A) are better oxidation agents than $\text{Pb}(\text{OAc})_4$. PhCHO is obtained in 88% yield from $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ and PhIO in $\text{H}_2\text{O} + \text{C}_6\text{H}_6$. *Ph iododi-(chloroacetate)*, decomp. 116°, and *-(dichloroacetate)*, decomp. 112°, are new; the di(trichloroacetate) could not be isolated. H. B.

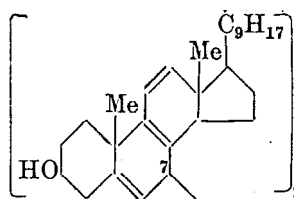
Photometric determination of oestrogens. I. Modified Kober reaction for determining total oestrogens in a mixture of oestrogenic steroids. II. New colour reaction for oestriol. C. BACHMAN (J. Biol. Chem., 1939, 131, 455—462, 463—468).—I. The total content of a mixture of oestrone, α -oestradiol, and oestriol can be determined using a modification of Kober's reaction (A., 1931, 1195).

II. A stable violet-pink colour produced by heating oestriol at 150° with *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ in H_3PO_4 is used to determine oestriol in the presence of oestrone.

E. M. W.

Constitution of dehydroergopinacone. T. ANDO (Bull. Chem. Soc. Japan, 1939, 14, 482—486).

Dehydroergopinacone (I) with $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$ yields the diacetate, m.p. 195—196.5° [opaque; clear at 200.5° (corr.) (decomp.)], $[\alpha]_D^{25} = -242^\circ$ in CHCl_3 , also formed from dehydroergosteryl acetate by irradiation with sunlight in EtOH-eosin and CO_2 , which is not



dehydrogenated by $\text{Hg}(\text{OAc})_2$. The absorption spectrum of (I) in C_6H_{14} shows a max. at 275 μ ., indicating that (I) has the annexed structure.

J. D. R.

Derivatives of cyclopentane. R. B. ROTHSTEIN and M. ROTHSTEIN (Compt. rend., 1939, 209, 761—762; cf. A., 1935, 474; 1936, 54).—*cyclopentene* [prep. (method: Fournau *et al.*, A., 1922, i, 639) in quant. yield from *cyclopentanol*] and $\text{NH}_3 \cdot \text{CO} \cdot \text{NHCl}$ in aq. AcOH give 60—70% of *trans*-2-chlorocyclopentanol, b.p. 81—82°/15 mm., which with aq. NaOH at room temp. affords epoxycyclopentane (I), b.p. 100—101°. The 2-hydroxycyclopentylalkylacetic acids obtained (cf. *loc. cit.*) from (I) and $\text{CNaAlk}(\text{CO}_2\text{Et})_2$ are dehydrated to odoriferous lactones [2-*keto*-3-*alkyl*-4:5-trimethylenetetrahydrofurans (A)] only at high temp. and ≤ 1 atm. The following (A) are described: *alkyl* = *Et*, b.p. 128°/14 mm., *Pr*^a, b.p. 141°/14 mm., *Bu*^a, b.p. 154°/16 mm., *Bu*^b, b.p. 148°/15 mm., and *isoamyl*, b.p. 163°/15 mm.

J. L. D.

Dihalogen-substituted α -amino- α -*p*-hydroxyphenylacetic acid.—See B., 1940, 86.

Study by means of the isotopes of nitrogen and hydrogen of the [*in vivo*] inversion of *d*- α -amino- γ -phenylbutyric acid and the acetylation of *l*- α -amino- γ -phenylbutyric acid. V. DU VIGNEAUD, (MISS) M. COHN, G. B. BROWN, O. J. IRISH, R. SCHOENHEIMER, and D. RITTENBERG (J. Biol. Chem., 1939, 131, 273—296).—In this inversion almost all the original N is shown, by use of ^{15}N , to be replaced by new N. $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ hydrogenated in 50% EtOH in presence of Pd and NH_3 containing 1.98 at.-% excess of ^{15}N (cf. Schoenheimer *et al.*, A., 1939, II, 144) gives *dl*- α -amino- γ -phenylbutyric acid (I) (containing 1.97 at.-% excess of ^{15}N), of which the *carbobenzyloxy*-derivative, m.p. 112°, is resolved by *d*- and *l*-phenylethylamine, giving the *d*-phenylethylamine salt, $[\alpha]_D^{25} +19.4^\circ$ in EtOH , of *carbobenzyloxy-l*-aminophenylbutyric acid, hydrolysed and reduced to *l*-(+)- α -amino- γ -phenylbutyric acid (II), $[\alpha]_D^{25} +48.4^\circ$ in N-HCl (containing 1.79 at.-% excess of ^{15}N), and the *l*-phenylethylamine salt, $[\alpha]_D^{25} -19.3^\circ$, of the *carbobenzyloxy*-derivative of *d*-(−)- α -amino- γ -phenylbutyric acid (III), $[\alpha]_D^{25} -48.2^\circ$ (containing 1.77 at.-% excess of ^{15}N) (cf. Rittenberg *et al.*, A., 1939, II, 235).

Rats fed with a fluid diet and 350 mg. per day of (I), (II), or (III) were also in certain experiments injected subcutaneously with D_2O , and fed sufficient D_2O to maintain its concn. in body fluids at ~2.5%. Those fed with (I) (1.97 at.-% excess of ^{15}N) excreted *l*-(+)- α -acetamido- γ -phenylbutyric acid (IV) (cf. du Vigneaud *et al.*, A., 1938, II, 98) containing ~1 at.-% excess of ^{15}N ; i.e., ~50% of the N in (IV) is original N of (I). Those fed with (II), (A) having $[\alpha]_D^{25} +35.5^\circ$, and containing 2.01 at.-% excess of ^{15}N , and (B) having $[\alpha]_D^{25} +48.4^\circ$, and containing 1.79 at.-% excess of ^{15}N , excreted (IV) containing ~1.45 at.-% excess of ^{15}N ; i.e., 72.7 and 81.4% respectively of the N of (IV) is original N of (II). Those fed with (III), (C) having $[\alpha]_D^{25} -44.2^\circ$, and containing 1.92 at.-% excess of ^{15}N , and (D) having $[\alpha]_D^{25} -48.2^\circ$, and containing 1.77 at.-% excess of ^{15}N , excreted (IV) containing 0.225 and 0.11 at.-% excess of ^{15}N ; i.e., only 11.7 and

6.3% of the N is original N of (III). [Material in (A) and (C) resolved through brucine, in (B) and (D) by new method described above.] In experiments (B) and (D), D_2O was also administered, and the resulting (IV) was hydrolysed to an acid containing 1 atom of D per mol. In an experiment in which (II) (no ^{15}N) and D_2O were fed, (IV) was excreted containing ~3.6 D per mol., hydrolysed to an acid (V) containing ~1 D per mol., which was degraded by chloramine-T to $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CHO}$ containing ~0.17 D per mol., showing that the D in (V) is in the α -position. Rats fed with *d*-(−)- α -acetamido- γ -phenylbutyric acid (VI) (no ^{15}N) and D_2O excrete (VI) containing no D.

It is suggested that (II) and (III) are dehydrogenated to $\text{NH} \cdot \text{CR} \cdot \text{CO}_2\text{H}$ (VII) ($\text{R} = \text{CH}_2\text{Ph} \cdot \text{CH}_2$), and this is converted either by AcCO_2H (VIII) into $\text{CO}_2\text{H} \cdot \text{CR} \cdot \text{N} \cdot \text{CMe}(\text{OH}) \cdot \text{CO}_2\text{H}$ and thus into $\text{CO}_2\text{H} \cdot \text{CHR} \cdot \text{NHAc}$ (IV), or by hydrolysis into $\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ and NH_3 (at which stage ^{15}N will be lost), and back into (VII) (cf. Braunstein *et al.*, A., 1937, II, 448; III, 210) and thus into (IV). If dehydrogenation of (III) is much more rapid than that of (II) (cf. Krebs, A., 1935, 1014), (VII) may be formed faster than (VIII) is available, so that hydrolysis will predominate. An alternative hypothesis, based on a qual. inability of (III) to be directly acetylated or to partake in transamination (cf. Braunstein, *loc. cit.*), is also considered.

E. W. W.

Condensation of aldehydes with amides. IV. *m*-Hydroxybenzaldehyde. R. K. MEHRA and K. C. PANDYA. V. *p*-Hydroxybenzaldehyde. M. MANZUR and K. C. PANDYA. VI. Condensation of *o*-, *m*-, and *p*-methoxybenzaldehydes. R. K. MEHRA and K. C. PANDYA (Proc. Indian Acad. Sci., 1939, 10, A, 279—281, 282—284, 285—288; cf. A., 1938, II, 363).—IV. *m*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ condenses with the requisite amide to *m*-hydroxybenzylidene-propionamide, m.p. 210°, -benzamide, m.p. 205°, and -phenylacetamide, m.p. 190°. Condensation occurs readily even in the absence of a condensing agent; a trace of $\text{C}_5\text{H}_5\text{N}$ or lutidines (I) does not materially increase the yield and appears to cause some resinification. Attempted condensations of NH_2Ac at 50° to 130° in absence of a condensing agent or in presence of $\text{C}_5\text{H}_5\text{N}$ or (I) cause much resinification and some aldehyde remains unchanged. A product could not be isolated from $\text{HCO} \cdot \text{NH}_2$.

V. *p*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ is condensed with the appropriate amide at 130—140° for 4—5 hr. in presence or absence of org. bases such as $\text{C}_5\text{H}_5\text{N}$ or piperidine, giving good yields (60—92%) of *p*-hydroxybenzylideneacetamide, decomp. 340° (decomp.), -formamide, decomp. 216°, -propionamide, decomp. 195°, -benzamide, becomes dark red at 190°, decomp. ~215°, and -phenylacetamide, m.p. >340°. They all decolorize Baeyer's reagent instantly and give a dark red colour with conc. H_2SO_4 . With conc. HCl they yield a pink colour which becomes deep rose on warming or keeping. They are decomposed by strong mineral acids with liberation of the original aldehyde.

VI. With *o*-, *m*-, or *p*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ and $\text{HCO} \cdot \text{NH}_2$ little or no condensation product is obtained at various temp. and in the presence or absence of an

org. base. The other amides all give substituted benzylidenediamides in 37% to 57% yield which is not considerably improved by the addition of a little org. base. The following are described: *o*-methoxybenzylidenebis-acetamide, m.p. 223°, -propionamide, m.p. 196—197°, -benzamide, m.p. 233°, and -phenylacetamide, m.p. 197°; *m*-methoxybenzylidenebis-acetamide, m.p. 206°, -propionamide, m.p. 201°, -benzamide, m.p. 201—202°, and -phenylacetamide, m.p. 181—182°; *p*-methoxybenzylidenebis-acetamide, m.p. 230—231°, -propionamide, m.p. 228°, -benzamide, m.p. 223—224°, and -phenylacetamide, m.p. 243°.

H. W.

3:5-Di-iodo-4-hydroxyhippuric acid and derivatives.—See B., 1940, 87.

Preparation of diethyl cyclobutane-1:1-dicarboxylate by Kishner's method. B. A. KAZANSKI (J. Gen. Chem. Russ., 1939, 9, 1568).—The low yield of Et₂ cyclobutanedicarboxylate (I) reported by Venus-Danilova (A., 1938, II, 393) following Kishner's instructions (A., 1905, i, 786) is ascribed to a misprint in Kishner's paper; using 1 g.-mol. of Cl[CH₂]₃Br per g.-mol. of CH₂(CO₂Et)₂ the yield of (I) is 50%, as obtained by Kishner.

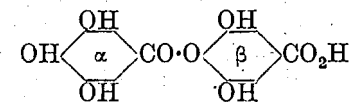
R. T.

Synthesis of phenanthrene derivatives. A. SCHÖNBERG and F. L. WARREN (J.C.S., 1939, 1838—1841; cf. A., 1939, II, 152).—*o*-C₆H₄Ph·COCl [from the acid and (COCl)₂ in C₆H₆ at 30°] and CH₂N₂ in Et₂O yield ω -diazo-*o*-phenylacetophenone, m.p. 106°, which, in dioxan, with Ag₂O in aq. Na₂S₂O₃ gives *o*-diphenylacetic acid, m.p. 116°, converted by AcOH-Ac₂O-ZnCl₂ into 9-phenanthryl acetate; hydrolysis (KOH-EtOH) then gives 9-hydroxyphenanthrene. Et *o*-diphenylacetate and Et₂C₂O₄ with KOEt in EtOH-Et₂O yield crude Et α -keto- β -2-diphenylsuccinate, which with H₂SO₄ at 100° gives phenanthrene-9:10-dicarboxylic anhydride.

J. D. R.

Abnormal osmotic effects with chain molecules. II. Synthesis and cryoscopic behaviour of polydepsides. F. KLAGES, F. KIRCHER, and J. FESSLER (Annalen, 1939, 541, 17—53; cf. A., 1935, 1355).— α -Trimethyl- β -diacetyl-di- (I), m.p. 218° (chloride,

m.p. 166°), α -trimethyl- β -tetra-acetyltri- (II), m.p. 223—224° (chloride, m.p. 167°), and α -trimethyl- β - γ -hexa-



acetyl-tetra- (III), m.p. 235°, -gallic acid (for nomenclature cf. annexed formula for digallic acid) are prepared by condensation (COMe₂ and aq. NaOH) of the appropriate acid chloride with 3:5-di-acetylgallic acid. Quinol di(trimethylgallate) (IV), m.p. 224°, di(triacetylgallate) (V), m.p. 250°, and di-(α -trimethyl- β -diacetyldigallate) (VI), m.p. 248°, and phloroglucinol tri(trimethylgallate) (VII), m.p. 180°, tri(triacetylgallate) (VIII), m.p. 210°, tri-(α -trimethyl- β -diacetyldigallate) (IX), softens 150—175°, and tri-(penta-acetyldigallate) (X), softens 150—175° (penta-acetyldigalloyl chloride, m.p. 173°), are obtained in an analogous way. All except (IX) and (X) are cryst. The cryoscopic behaviour of the compounds in dioxan, AcOH, and CHBr₃ has been investigated over the concn. range 0.025—1%. In dioxan (I), (VII),

(VIII), and (X) behave normally, whilst the others give f.p. depressions > those calc. from the formulæ. The deviation is greatest at low concns., and in the case of (VI) amounts to 5 times the theoretical val. In AcOH only (I), (VII), and (VIII) are normal. In CHBr₃ all the substances give normal vals. The anomalies, which depend on the mol. form rather than on the chemical nature of the solute, are generally associated with a straight chain of at least 3 rings; branched mols. [(VII)–(X)] give abnormal results only when the branches themselves contain a 3-ring chain. (II), (III), (IV), (V), and (VI) in dioxan, and (II), (III), and (V) in AcOH, behave osmotically as though the ring units constituting the mols. were independent mols. The observed behaviour of CHBr₃ supports the suggestion previously put forward, that anomalies are found only in solvents having a mol. wt. < that of the ring unit concerned. Possible explanations are discussed.

F. L. U.

Ellagic tannins.—See A., 1940, III, 175.

Aldehydes and hydroxy-aldehydes of the polymethylene series. VIII. Isomeric transformations of cyclobutanealdehyde. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1938, 8, 1179—1191).—cyclobutanealdehyde (I) with H₂SO₄ on pumice at 130—135° yields cyclopentanone (II). (I) or (II) and Br in CS₂ give a Br-derivative (not isolated), converted by heating with an aq. suspension of BaCO₃ into 2-hydroxycyclopentanone, b.p. 104—108°/25 mm. (p-nitrophenylhydrazine, m.p. 157—158°), which with semicarbazide yields 3-keto-5:6-trimethylene-2:3:4:5-tetrahydro-1:2:4-triazine, decomp. 194°.

R. T.

Autoxidation of benzaldehyde in presence of 7:8-diphenylacenaphthylene. G. WITTIG and K. HENKEL (Annalen, 1939, 542, 130—144).—7:8-Diphenylacenaphthylene (I), m.p. 161—162° [prep. (cf. A., 1931, 1415) from *cis*- (II) or *trans*- (III) 7:8-dihydroxy-7:8-diphenylacenaphthene and NaI in COMe₂ saturated with HCl], is stable to light and air in non-polar solvents and [unlike didiphenylene-ethylene (A., 1939, II, 22)] is very stable to O₂ in polar solvents (dioxan). When shaken with O₂ in presence of PhCHO and CCl₄, (I) is autoxidised to (*cis*)-7:8-dihydroxy-7:8-diphenylacenaphthene CHPh ether (IV), m.p. 249—249.5°; autoxidation of the PhCHO is thereby retarded to a degree approx. \propto concn. of (I). Autoxidation of PhCHO in CCl₄ in absence or presence of (I) is accelerated by light to approx. the same extent in each case. Autoxidation of PhCHO in CCl₄ is also retarded by (II), (III), (IV), or C₁₀H₈. It is unlikely that BzO₂H is produced in the reaction or that an intermediate such as CPh·O·O·CHPh·OH or CHPh<O·O>CPh·OH is formed (from BzO₂H and PhCHO) (cf. below). The active agent is considered to be the peroxide CHPh<O·O> (cf. loc. cit.). All experiments are carried out at 20°.

Successive treatment of *cis*- or *trans*-(I) with LiMe (in Et₂O and N₂) and CHPhCl₂ (at 100° in sealed tube) and of (II) or (III) with CKPhMe₂ and CHPhCl₂ gives 1:8-C₁₀H₆Bz₂ (V) in each case. BzO₂H (1 mol.) has no action on (I) in CHCl₃ at 0°/3 days; a large

excess in CHCl_3 at 25° affords (V), which is also produced from (I) (1 mol.), BzO_2H (10 mols.), and PhCHO (10 mols.) in CHCl_3 and N_2 at 25° . Stilbene and α -chlorostilbene ozonides have no action on (I). (IV), which is also obtained from (II) or (III) and $\text{PhCHO}\cdot\text{HCl}$, is hydrolysed ($\text{AcOH}\cdot\text{HCl}$) to PhCHO and 7 : 7-diphenylacenaphthen-8-one. H. B.

Characterisation of opianic acid. A. S. TSCHERNISCHEV (J. Gen. Chem. Russ., 1938, 8, 1254).—Certain data referring to the solubility of opianic acid (I) in H_2O and org. solvents, given in Beilstein's Lexicon, are corr. In EtOH , (I) gradually yields a ψ -Et ester. R. T.

γ -Substituted resorcinol derivatives. II. Synthesis of 3-aldehydoresacetophenone, 3-acetyl- β -resorcylaldehyde, and 2 : 3 : 6-trihydroxyacetophenone. K. NAKAZAWA (J. Pharm. Soc. Japan, 1939, 59, 107—110; cf. A., 1939, II, 427).—1 : 2 : 4- $\text{C}_6\text{H}_3\text{Ac}(\text{OH})_2$ and $\text{AlCl}_3\cdot\text{Zn}(\text{CN})_2\cdot\text{Et}_2\text{O}$, with HCl give 3-aldehydo-2 : 4-dihydroxyacetophenone, m.p. 106—107° [monoxime, m.p. 222°; dioxime, m.p. 226° (decomp.)], oxidised by H_2O_2 in $\text{N}\cdot\text{NaOH}$ to gallacetophenone. Similarly, 1 : 2 : 6- $\text{C}_6\text{H}_3\text{Ac}(\text{OH})_2$ yields 3-aldehydo-2 : 6-dihydroxyacetophenone, m.p. 100° (monoxime, m.p. 171°; dioxime, m.p. 179°), oxidised to 2 : 3 : 6-trihydroxyacetophenone (triacetate, m.p. 96°; tribenzoate, m.p. 186°). J. D. R.

Cobalt salts of glyoximes. V. L. CAMBI and L. MALATESTA (Gazzetta, 1939, 69, 547—561; cf. A., 1936, 825).— α -Diphenylglyoxime (I) with CoBr_2 in EtOH , exposed to the air, followed by conc. HBr , gives a salt $[\text{Co}(\text{RH})_2\text{Br}_2]\text{H}$ (II) [$\text{RH}_2 = (\text{OH}\cdot\text{N}\cdot\text{CPh})_2$], converted by hot $\text{KOAc}\cdot\text{EtOH}$ into the hydrate, $[\text{Co}(\text{RH})_2(\text{OH})_2]\text{H}$ (+ H_2O). With $\text{Co}(\text{OAc})_2$ in COMe_2 , (I) gives the compounds $[\text{Co}^{\text{II}}(\text{RH})_2]$ and $[\text{Co}^{\text{III}}(\text{RH})_2\text{OH}]$ (converted into the anhydrous compound, $[\text{CoR}_2\text{H}]$). A $\text{NH}(\text{CH}_2\text{Ph})_2$ salt derived from (II) in which Br is partly replaced by OH is obtained. α -Phenylglyoxime (III) in EtOH with aq. HBr at 60—70°, followed by CoBr_2 slowly added, with passage of air, gives the salt $[\text{Co}(\text{R}'\text{H})_2\text{Br}_2]\text{H}$ (IV) [$\text{R}'\text{H}_2 = \text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$]. With $\text{NH}(\text{CH}_2\text{Ph})_2$ (=M), (IV) gives the compound $[\text{Co}(\text{R}'\text{H})_2\text{MBr}]\text{H}$. (IV) with $\text{KOAc}\cdot\text{EtOH}$, washed with H_2O , gives the hydrate $[\text{Co}(\text{R}'\text{H})_2(\text{OH})_2]\text{H}$. With CoBr_2 in EtOH at 50—60°, (III) gives a product regarded as $[\text{Br}_2\text{Co}^{\text{III}}(\text{R}'\text{H})_2]\text{Co}^{\text{II}}(\text{R}'\text{H})_2\text{Co}^{\text{III}}\text{Br}(\text{OH})$ (V) (+6 EtOH). This with $\text{EtOH}\cdot\text{NH}_3$ yields the compound $[\text{Co}_3\text{R}'_4(\text{NH}_3)_4(\text{HBr})_2]$ (+4 H_2O), which with aq. $\text{AcOH}\cdot\text{HBr}$ gives the bromide $[\text{Co}(\text{R}'\text{H})_2(\text{NH}_3)_2]\text{Br}$ (corresponding nitrate, perchlorate, persulphate, and H phosphate prepared). In boiling H_2O , (V) gives the compound $[\text{Co}(\text{R}'\text{H})_2\text{Br}(\text{OH})]\text{H}$. In boiling $\text{C}_5\text{H}_5\text{N}$ (=M'), (V) gives the compounds $[\text{Co}(\text{R}'\text{H})_2\text{M}'\text{Br}]$ (VI), and $[\text{Co}(\text{R}'\text{H})_2\text{M}'\text{Br}]\text{CoBr}_2$ [which in H_2O gives (VI)]. In hot $\text{KOAc}\cdot\text{EtOH}$, (V) gives the compound $[\text{Co}_3(\text{R}'\text{H})_4(\text{OH})_4]\cdot 4\text{H}_2\text{O}$. In EtOH , (III) and $\text{Co}(\text{OAc})_2$ give the compound $[\text{Co}^{\text{II}}\text{R}_2']$. α -Benzoylmethylglyoxime and $\text{CoBr}_2\cdot\text{EtOH}$, exposed to air, with conc. HBr give compounds, $[\text{Co}(\text{R}'\text{H})_4\text{Br}_2(\text{OH})_2]\text{H}_2$ (VII) and $[\text{Co}(\text{R}'\text{H})_2\text{Br}(\text{OH})]\text{H}$ [$\text{R}'\text{H}_2 = \text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CBz}\cdot\text{N}\cdot\text{OH}$]. In boiling H_2O , (VII) gives a hydrate ($\text{Co} : \text{N} = 1 : 3$). The magnetic susceptibility of these compounds is determined, and

the structure of compounds of the Co^{II} and Co^{III} series is discussed. E. W. W.

Action of oxalyl chloride on phenolic ethers. P. C. MITTER and H. MUKHERJEE (J. Indian Chem. Soc., 1939, 16, 393—395).— $(\text{COCl})_2$ (I) and $\text{PhOMe}\cdot\text{AlCl}_3\cdot\text{CS}_2$ give 4 : 4'-dimethoxybenzil, oxidised by $\text{H}_2\text{O}_2\cdot\text{AcOH}$ at 70—80° to $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ and (I) similarly give 4 : 4'-dimethoxy-3 : 3'-dimethylbenzil, m.p. 174°, converted by NaOH at 180° into the benzoic acid, m.p. 145—147°, or oxidised to 4 : 3 : 1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$. (I) and m - or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ give only (?) 6- or 5-methylsalicylic acid, respectively. $o\text{-C}_6\text{H}_4(\text{OMe})_2$ gives 3 : 4 : 1- $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}_2\text{H}$. (I) and $m\text{-C}_6\text{H}_4(\text{OMe})_2$ or 1 : 2 : 3- $\text{C}_6\text{H}_3(\text{OMe})_3$ give no pure product and $p\text{-C}_6\text{H}_4(\text{OMe})_2$ does not react. A. T. P.

Biochemical preparation of inosose.—See A., 1940, III, 75.

Catalysed condensation reactions. M. P. MASINA (J. Gen. Chem. Russ., 1939, 8, 1264—1271).—*cyclo*Hexanol passed over 13 : 87 Co-Th catalyst at 380° or over 7 : 3 Ni-Th catalyst at 380—450° yields chiefly 2-*cyclohexylidenecyclohexanone*. This is also obtained similarly from *cyclohexanone* (I) or (I)-*cyclohexane* (II) mixtures, but not from (II) alone. The most active catalysts are obtained by pptn. from nitrate solutions with K_2CO_3 . R. T.

Synthesis of cyclopentanone-2 : 5-dicarboxylic ester. S. N. NAUMOV and L. P. DANILEVSKI (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 29, 4 pp.).— Et_3 butane- $\alpha\alpha$ -tricarboxylate and NaOEt in EtOH (5 hr. at 40°, then 5 hr. at the b.p.) yield Et_2 cyclopentanone-2 : 5-dicarboxylate, b.p. 165—166°/13 mm. [*semicarbazone*, m.p. 200—201° (decomp.); ? *phenylhydrazone*, m.p. 79°]. R. T.

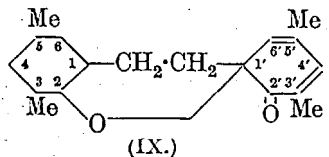
Quinonemethides. K. FRIES and E. BRANDES (Annalen, 1939, 542, 48—77).—All attempts to obtain a 4-methylene- $\Delta^{2:5}$ -*cyclohexadienone* (quinonemethide) have proved unsuccessful. 4-Hydroxy-3 : 5-dimethylbenzyl bromide (I), m.p. 103—105° (decomp.) [*Ac* derivative (II), m.p. 68—69°], from the alcohol and HBr in C_6H_6 at 50°, could not be obtained pure. When treated with various solvents (MeOH , EtOH , H_2O , or aq. COMe_2 at room temp.) or reagents (NaOH , NaOEt , $\text{SnCl}_2\cdot\text{AcOH}$), 2 mols. of (I) eliminate CH_2Br_2 and give 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylmethane (III). The diacetate of (III) is similarly obtained from (II) and Cu powder in indifferent solvents, Zn dust- $\text{HCl}\cdot\text{COMe}_2$, and Zn dust, anhyd. NaOAc , or AgOAc in Ac_2O . Mesitol is formed from (I), but not from (III), by distillation with Zn dust. Aq. NaOAc (2 mols.) and (I) (1 mol.; in C_6H_6) give 4-(4'-hydroxy-3' : 5'-dimethylbenzylidene)-2 : 6-dimethyl- $\Delta^{2:5}$ -*cyclohexadienone* (IV), m.p. 172—173°, the violet 3 : 5 : 3' : 5'-tetramethylstilbene-4 : 4'-quinone (V), +0.25 H_2O , m.p. 215° (from CHCl_3), m.p. (anhyd. from $\text{C}_5\text{H}_5\text{N}$) 330° (brown and then black at 220—230°), and 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldibenzyl, m.p. 166—167° (diacetate, m.p. 150—151°); the formation of (III) [and thence (IV)] and 2 : 6-dimethyl-4-methylene- $\Delta^{2:5}$ -*cyclohexadienone* (undergoes dimerisation; acts as a dehydrogenating agent) is postulated. Reduction

(Zn dust, AcOH) of (V) affords 4:4'-*dihydroxy*-3:5:3':5'-*tetramethylstilbene*, m.p. 239—240° (diacetate, m.p. 237—238°), which is oxidised (HNO₃-EtOH) to (V). Impure αβ-*dibromo*-4:4'-*dihydroxy*-3:5:3':5'-*tetramethyldibenzyl*, m.p. 176° (decomp.) [from (V) and HBr in C₆H₆], is converted by H₂O (slowly) or dil. NaOH (rapidly) into (V). Reduction (Zn dust, AcOH) of (IV) gives (III); with aq. COMe₂ and AcOH, (IV) affords 4:4'-*dihydroxy*-3:5:3':5'-*tetramethyldiphenyl-carbinol*, m.p. 156—158° (decomp.) [triacetate (VI), m.p. 139—140°, also from (IV) and Ac₂O—conc. H₂SO₄], and -*carbinyl acetate*, m.p. 155—160° (decomp.), respectively. AcOH-HBr converts (IV) into a deep violet compound, C₁₇H₁₉O₂Br.H₂O, m.p. 245—248° (decomp.) (structure discussed), which with Ac₂O-H₂SO₄ yields (VI).

4-Bromo-2:4:6-trimethyl-Δ^{2:5}-cyclohexadienone (VII) [from AcOH-Br and mesitol in aq. AcOH-NaOAc at -3°] rearranges rapidly to (I). Treatment of a freshly prepared solution of (VII) with H₂O gives an oil which when distilled (vac.) undergoes partial decomp.; mesitol, (III), and a ? *dihydroxytetramethyldibenzyl*, m.p. 153° (purified through its diacetate, m.p. 133°), are isolated from the distillate. 3:4:5-Tribromo-2:4:6-trimethyl-Δ^{2:5}-cyclohexadienone, m.p. 80—84° (decomp.) [from dibromomesitol; as for (VII)] (rearranges slowly at room temp. and rapidly when heated to 4:3:5:2:6:1-OH·C₆Me₂Br₂·CH₂Br), and NH₂Ph in EtOH + NaOAc at 0—20° afford the 3:5-*dibromo*-4-*anilino*-derivative, m.p. 136°, which is rearranged by AcOH—conc. HCl to 3:5-*dibromo*-4'-*amino*-2:4:6-trimethyldiphenyl ether, m.p. (hydrochloride, m.p. 298°; Ac derivative, m.p. 233°).

[With F. STRUFFMANN.] 2-Hydroxy-3:5-dimethylbenzyl bromide, m.p. 73° (from the alcohol and HBr in C₆H₆ + CaCl₂), resembles the chloride (A., 1907, i, 613). 2:3:5:1-OAc·C₆H₂Me₂·CH₂Cl, b.p. 151°/15 mm., m.p. 30°, and Cu powder in boiling C₆H₆ give the diacetate, m.p. 125°, of 2:2'-*dihydroxy*-3:5:3':5'-*tetramethyldibenzyl* (VIII), m.p. 167°.

Oxidation [K₂Fe(CN)₆, aq. KOH] of (VIII) affords 2'-*keto*-2:1'-*oxido*-3:5:3':5'-*tetramethyl-1':2'-dihydrodibenzyl* (IX), m.p. 123° [reduced (Zn dust, AcOH) to (VIII)], whilst the



Br₄-derivative (X) (*loc. cit.*) of (VIII) similarly yields 4:6:4':6'-*tetrabromo*-2'-*keto*-2:1'-*oxido*-3:5:3':5'-*tetramethyl-1':2'-dihydrodibenzyl* (XI), m.p. 168° [reduced to (X)], and not a quinonemethide (*cf. loc. cit.*; Pummerer *et al.*, A., 1919, i, 439). EtOH-NHPh·NH₂ and -NH₂Ph with (XI) give the corresponding 4:6:6'-*tribromo*-4'-*phenylhydrazino*-, m.p. 193° (Ac₂ derivative, m.p. 221°), and 4'-*anilino*-derivative, m.p. 206° (decomp.), respectively. 3:5-Di(bromomethyl)-*p*-cresol in Et₂O with 2N-Na₂CO₃ affords a trimeride, m.p. 167°, of 4-methyl-2-bromomethyl-6-methylene-Δ^{2:4}-cyclohexadienone, whilst 2:6-dibromo-3:5-di(bromomethyl)-*p*-cresol in Et₂O with 10% aq. NaOAc gives 4:6:4':6'-*tetrabromo*-2'-*keto*-2:1'-*oxido*-5:5'-*dimethyl-3:3'-di(bromomethyl)-1':2'-dihydrodibenzyl* (XII), m.p. 194°. Energetic reduction (Zn dust, AcOH—conc. HCl) of (XII) yields

(X), whilst AcOH-HBr at 115—120° (sealed tube) converts it into 4:6:4':6'-*tetrabromo*-2:2'-*dihydroxy*-5:5'-*dimethyl-3:3'-di(bromomethyl)dibenzyl*, m.p. 228° (diacetate, m.p. 290°), which with boiling MeOH gives the 3:3'-*di(methoxymethyl)* derivative, m.p. 191°. Mesitol is most conveniently prepared by reduction (Zn dust, COMe₂—conc. HCl) of the acetate, m.p. 108°, of 3:5-di(chloromethyl)-*p*-cresol. H. B.

cycloHexane-1:2-dione. S. N. NAUMOVA and O. A. VOLODINA (*Acta Univ. Asiæ Mediæ*, 1937, [vi], No. 20, 8 pp.).—Et₂ 2:3-diketocyclohexane-1:4-dicarboxylate and 10% H₂SO₄ (4—7 hr. at the b.p.) yield cyclohexane-1:2-dione (I), b.p. 75—76°/9 mm., m.p. 33—34°, rapidly changing to a glassy substance when exposed to air and light, and this product yields crystals of a *hydrate*, C₆H₈O₂·0.5H₂O, m.p. 128°, after long keeping. (I) is not identical with Wallach's "diosphenol" (A., 1924, i, 862); it does not yield adipic acid when oxidised, nor does it give the osazone and phenylurethane described by Wallach. The hydrate, m.p. 128°, yields adipic acid when oxidised with KMnO₄. R. T.

Action of bromine on cyclohexane-1:4-dione and its homologues. S. N. NAUMOV and Z. I. EMMANUILOVA (*Acta Univ. Asiæ Mediæ*, 1937, [vi], No. 15, 7 pp.).—Bromination of cyclohexane-1:4-dione or its 2:5-Me₂ derivative in presence or absence of H₂O, C₅H₅N, or NaHCO₃, at 0° or at room temp., did not yield Br-derivatives, but only tarry products. A mixture, m.p. 94—100°, of Br₂-derivatives of undetermined structure was obtained from Et₂ 2:5-diketo-1:4-dimethylcyclohexane-1:4-dicarboxylate. R. T.

Action of sodium ethoxide on 2:3-diketocyclopentane-1:4-dicarboxylic ester. S. N. NAUMOV and S. L. GUSINSKAJA (*Acta Univ. Asiæ Mediæ*, 1937, [vi], No. 23, 10 pp.).—Et₂ 2:3-diketocyclopentane-1:4-dicarboxylate (I) is recovered unchanged after treatment with NaOEt in EtOH. (I) (in EtOH-NaOEt) with MeI gives Et₂ 2:3-diketo-1-methylcyclopentane-1:4-dicarboxylate, b.p. 189—190°/12—14 mm. [Na salt (II), m.p. 172°; phenylhydrazone, m.p. 170—170.5°], also not reacting with NaOEt in EtOH. A C₆H₆ suspension of (II) with MeI yields a substance, b.p. 190°/15 mm., isomeric with the Me₂ derivative of (I), but not reacting with CO group reagents. R. T.

(A) Condensation of adipic and oxalic esters. S. N. NAUMOV and L. S. DEDUSENKO. (B) Condensation product, C₁₆H₂₀O₉, of adipic with oxalic ester. S. N. NAUMOV and Z. I. EMMANUILOVA. (C) Mutual transformations of 2:3-diketocyclohexane-1:4-dicarboxylic ester and 2-hydroxycyclopentane-1:2:3-tricarboxylic ester. S. N. NAUMOV and L. S. DEDUSENKO (*Acta Univ. Asiæ Mediæ*, 1937, [vi], No. 16, 8 pp.; No. 18, 5 pp.; No. 22, 10 pp.).—(A) Et₂ adipate and Et₂C₂O₄ in EtOH-NaOEt at 40° yield Et₂ 2:3-diketocyclohexane-1:4-dicarboxylate (I), Et₂ Δ¹-cyclopentene-1:2:3-tricarboxylate (II), Et cyclopentanone-2-carboxylate, and Et₃ oxaloadipate.

(B) In presence of excess of Et₂C₂O₄, and at 75—85°, a dicyclic substance, C₁₆H₂₀O₉, m.p. 117°, is obtained, in addition to the above four products. This

substance is hydrolysed by H_2O at room temp. to $\text{H}_2\text{C}_2\text{O}_4$, EtOH , and a substance, m.p. 155° , whilst with 5% aq. Na_2CO_3 the product is (II); with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ it gives a "dihydroxyquinoxaline" and Et 2-hydroxycyclopentane-1:2:3-tricarboxylate (III).

(c) The reaction (I) \rightarrow (III) takes place when (I) is treated with NaOEt in EtOH ; (III) is converted into (I) by Na and NaOEt in absence of EtOH . Under these conditions the reaction (III) \rightarrow (II) does not take place.

R. T.

Action of bromine on 2:3-diketocyclohexane-1:4-dicarboxylic ester. S. N. NAUMOV and V. V. LAVRENOVA (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 19, 6 pp.).— Et_2 2:3-diketocyclohexane-1:4-dicarboxylate and Br in CHCl_3 yield Et_2 1-bromo-, m.p. $51\text{--}52^\circ$, and Et_2 1:4-dibromo-2:3-diketocyclohexane-1:4-dicarboxylate, m.p. $84\text{--}86^\circ$; these eliminate HBr and Br_2 , respectively, when heated at 100° in vac., to yield 2:3:1:4-(OH) $_2\text{C}_6\text{H}_2(\text{CO}_2\text{Et})_2$ in both cases.

R. T.

Transformation of 2:3-diketocyclohexane-1:4-dicarboxylic ester when exposed to sunlight. S. N. NAUMOV and M. A. ZAKUTSKAJA (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 21, 13 pp.).—Exposure of Et_2 2:3-diketocyclohexane-1:4-dicarboxylate (I) to sunlight leads to formation of various products, including a dimeride, m.p. $78\text{--}80^\circ$, readily regenerating (I) when dissolved in EtOH , H_2O , aq. Na_2CO_3 , or aq. KOH , and a dimeride, m.p. $125\text{--}126^\circ$, not dissociating in EtOH , H_2O , or aq. Na_2CO_3 , nor reacting with PhNCO , $\text{NHPh}\cdot\text{NH}_2$, NH_2OH , or semicarbazide, but hydrolysed by 25% H_2SO_4 to two acids, $\text{C}_{14}\text{H}_{14}\text{O}_7$, m.p. $197\text{--}198^\circ$, and $\text{C}_{14}\text{H}_{16}\text{O}_8$, m.p. $174\text{--}175^\circ$, of undetermined structure.

R. T.

(A) 2:3-Diketo-1-methylcyclohexane-1:4-dicarboxylic ester. S. N. NAUMOV and R. J. DANTUSCHEVSKAJA. (B) 2:3-Diketo-1:4-dimethylcyclohexane-1:4-dicarboxylic ester. S. N. NAUMOV and N. S. VOLKENSCHTEIN (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 25, 4 pp.; No. 26, 6 pp.).—(A) The Na salt of Et_2 2:3-diketocyclohexane-1:4-dicarboxylate in C_6H_6 and MeI yield Et_2 2:3-diketo-1-methylcyclohexane-1:4-dicarboxylate (I), b.p. $183^\circ/11\text{ mm.}$, m.p. $49\text{--}50^\circ$ [oxime, m.p. $46\text{--}48^\circ$; compound with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 88°].

(B) The Na salt of (I) does not yield the expected 1:4- Me_2 derivative when treated with Me_2SO_4 or MeI , under various conditions. This failure is related to isomerisation of (I) to a non-ketonic form in presence of NaOEt .

R. T.

Product of reaction of succinylsuccinic with orthoformic ester. S. N. NAUMOV and C. E. FEIGELMAN (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 30, 6 pp.).— Et_2 succinylsuccinate and $\text{CH}(\text{OEt})_3$ in Ac_2O (3 hr. at the b.p.) yield Et_2 2:5-diketo-1:4-di(diethoxymethyl)cyclohexane-1:4-dicarboxylate, m.p. $84\text{--}89^\circ$ (bispirazolone from $\text{NHPh}\cdot\text{NH}_2$, m.p. 165°).

R. T.

Condensation of pimelic with oxalic ester. S. N. NAUMOV and A. N. PERMINOVA (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 28, 10 pp.).— $\text{Et}_2\text{C}_2\text{O}_4$ and Et_2 pimelate in $\text{NaOEt}\text{--EtOH}$ yield Et_2 2:3-diketo-cycloheptane-1:4-dicarboxylate, m.p. $70\text{--}71^\circ$ [phenyl-

hydrazone, m.p. $189\text{--}190^\circ$; compound with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 142°], and Et_3 α -oxalopimelate, b.p. $194\text{--}197^\circ/18\text{ mm.}$; the yield of the latter falls, and of the former rises, as the reaction temp. is raised from 20° to 115° .

R. T.

Diphensuccindene series. XVI. Derivatives of Δ^{10} -diphensuccindene-9:12-dione. K. BRAND and H. W. STEPHAN (Annalen, 1939, 542, 29–34).—10-Bromodiphensuccindene-9:12-dione (I) (A., 1937, II, 24) with $\text{NH}_2\text{OH}\cdot\text{HCl}$ or $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ in EtOH + a little conc. HCl gives the dioxime, m.p. $273\text{--}273.5^\circ$ (decomp.), or bisphenylhydrazone, m.p. 242° (decomp.), respectively, of Δ^{10} -diphensuccindene-9:12-dione [bis-*p*-nitrophenylhydrazone, m.p. 305.5° ; from (I) and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in boiling PhNO_2]; the compound, $\text{C}_{31}\text{H}_{16}\text{O}_3$ (loc. cit.), is not produced.

H. B.

Steroid ketones.—See B., 1940, 86, 87.

Sterols. XVIII. Δ^5 -Androsten-17-ol-7-one. S. KUWADA and K. TUTTHASI (J. Pharm. Soc. Japan, 1939, 59, 115–117).—*trans*-Dehydroandrosterone in Et_2O with CaCO_3 and SOCl_2 yields 3-chloroandrosten-17-one, m.p. 154° , reduced by $\text{Na}\text{--EtOH}$ to Δ^5 -androsten-17-ol (I). Oxidation of the acetate of (I) with CrO_3 in AcOH yields 17-acetoxy- Δ^5 -androsten-7-one (II), m.p. $212\text{--}213^\circ$ (oxime, decomp. $128\text{--}131^\circ$), which is hydrolysed by $\text{KOH}\text{--MeOH}$ to Δ^5 -androsten-17-ol-7-one, m.p. $143\text{--}144^\circ$. (II) appears to have slight physiological activity.

J. D. R.

Mol. compound (1:1), m.p. $191\text{--}192.5^\circ$, of cholesterol and urane-3(β):11-diol. 3-Deoxy-11-ketoequilenin (?), $\text{C}_{18}\text{H}_{16}\text{O}_2$, m.p. $212\text{--}214^\circ$ [semicarbazone, m.p. $255\text{--}260^\circ$ (decomp.)]. Trione, $\text{C}_{21}\text{H}_{30}\text{O}_3$, m.p. $127\text{--}129^\circ$ (disemicarbazone, + $0.5\text{H}_2\text{O}$, m.p. $>300^\circ$).—See A., 1940, III, 32.

Reaction of benzoquinone dibromide with ketones. S. N. NAUMOV and Z. N. NAZAROVA (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 14, 3 pp.).—Benzoquinone dibromide (I) reacts with certain ketones (COMe_2 , COMeEt , COEt_2 , COMePr , COPhMe , cyclohexanone), to yield quinol and α -bromo-ketones. $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ does not react with (I). Addition of Br to $\text{C}\cdot\text{C}$ is observed in the case of $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$.

R. T.

Behaviour of halogen atoms (A) of *p*-benzoquinone di- and tetra-bromides. S. N. NAUMOV and E. V. LEONTEVA, (B) of dichloride and dibromide of toluquinone. S. N. NAUMOV and L. A. BOGOLJUBOVA (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 12, 5 pp.; No. 13, 7 pp.).—(A) *p*-Benzoquinone dibromide (I) in EtOH and aq. KI react as follows: (I) + $2\text{KI} \rightarrow$ benzoquinone (II) + 2KBr + 2I . In presence of H_2SO_4 the further reaction (II) + H_2SO_4 + $2\text{KI} \rightarrow$ quinol + K_2SO_4 + 2I takes place. *p*-Benzoquinone tetrabromide reacts analogously, with liberation of 4 or 6 atoms of I , in neutral and acid solution, respectively.

(B) Toluquinone dibromide reacts analogously to (I) with KI . Elimination of HCl (1 mol.) from toluquinone dichloride occurs under the same conditions, so that only 1 or 2 atoms of I are liberated, in neutral

or acid solution, respectively, with production of 50 or 100%, respectively, of 1:4:2:5- $C_8H_2MeCl(OH)_2$.
R. T.

Kinetics of reaction of 2-chloroanthraquinone with aqueous ammonia.—See A., 1940, I, 31.

Semiquinone formation by anthraquinone and simple derivatives. A. GEAKE and J. T. LEMON (Trans. Faraday Soc., 1938, **34**, 1409—1427).—Redox titrations of aq. or aq. C_6H_5N solutions of anthraquinone, Na anthraquinone-2-sulphonate, 1-mono- and 1:4-di-benzamidoanthraquinone, and Caledon Red BN show that in every case oxidation occurs in two stages with the formation of a semiquinone as a sol. intermediate compound. Semiquinone formation is promoted by addition of org. solvents and by the presence of NHBz and naphthacridone groups.

F. L. U.

Products of condensation of cyclones with *p*-benzoquinone and α -naphthaquinone. E. A. ARBUZOV, V. S. ABRAMOV, and J. B. DEVJATOV (J. Gen. Chem. Russ., 1939, **9**, 1559—1563).—Cyclone and acecyclone do not react with *p*-benzoquinone (I) or α -naphthaquinone (II). Phenyclone (III) and (II) in $PhNO_2$ (4 hr. at 100°, or 12 hr. at room temp.) yield 1:4-endocarbonyl-1:4-diphenyl-2:3-(*oo'*-diphenylene)-11:12-dihydroanthraquinone, m.p. 265—267°, converted by boiling with $PhNO_2$ for 6 hr. into 1:4-diphenyl-2:3-(*oo'*-diphenylene)anthraquinone, m.p. 359°. With (I), (III) yields similarly 5:8-endocarbonyl-5:8-diphenyl-6:7-(*oo'*-diphenylene)-9:10-dihydro-1:4-naphthaquinone (IV), m.p. 194°, and 5:8-diphenyl-6:7-(*oo'*-diphenylene)-1:4-naphthaquinone, m.p. 405—408°; (IV) condenses further with (III), to give 1:4:5:8-diendocarbonyl-1:4:5:8-tetraphenyl-2:3:6:7-di-(*oo'*-diphenylene)-11:12:13:14-tetrahydroanthraquinone, m.p. 310°, and 1:4:5:8-tetraphenyl-2:3:6:7-di-(*oo'*-diphenylene)anthraquinone, m.p. 460—461°.
R. T.

Thujone series. VIII. Syntheses of isothujone. P. C. GUHA and A. KUPPUSAMI (J. Indian Inst. Sci., 1939, **22**, A, 249—254).—Successive additions of $CHPr^aAc \cdot CO_2Et$ and $CH_2Br \cdot CO_2Et$ to NaOEt in EtOH give *Et* β -carbethoxy- β -isopropyl-lævulate, b.p. 57°/20 mm., transformed by Zn and $CHMeBr \cdot CO_2Et$ in dry C_6H_6 into *Et* γ -hydroxy- β -carbethoxy- $\gamma\delta$ -dimethyl- β -isopropyladipate (I), b.p. 102—103°/25 mm., and an unidentified compound, b.p. 168°/23 mm. (I) does not give a definite product when acted on by mol. Na in boiling C_6H_6 whereas in xylene at 160° it is slowly transformed into 3-hydroxy-2:3-dimethyl-4-isopropylcyclopentanone, m.p. 63—64°. This is dehydrated by P_2O_5 in boiling C_6H_6 to isothujone, b.p. 224—228° (oxime, m.p. 117°).
H. W.

Addition of magnesium iodide to camphor and terpene derivatives. S. T. BOWDEN and T. F. WATKINS (J.C.S., 1939, 1961).— MgI_2 in Et_2O forms additive compounds with camphor, $5C_{10}H_{16}O \cdot 2MgI_2 \cdot Et_2O$, m.p. 108°, congealed, then m.p. 176°; carvone, $2C_{10}H_{14}O \cdot MgI_2 \cdot Et_2O$, m.p. 85°, congealed, then m.p. 125°; and santonin, $2C_{15}H_{18}O_3 \cdot MgI_2$, decomp. 175°.
F. R. S.

Camphane series. V. Synthesis of Manasse's ketonic acid, $C_{10}H_{16}O_3$, from camphorquinone:

2:2:3-trimethylcyclohexan-4-onecarboxylic acid. P. C. GUHA and D. D. GUPTA (J. Indian Inst. Sci., 1939, **22**, A, 255—262).— $Et_2 \alpha$ -cyanoglutarate, obtained by successive additions of $CN \cdot CH_2 \cdot CO_2Et$ and $CHMeBr \cdot CO_2Et$ to KOEt in EtOH, is condensed with $CMe_2C(CO_2Et)_2$ and the product is treated with MeI, thereby giving *Et* γ -cyano- $\alpha\gamma$ -dicarbethoxy- $\alpha\beta\beta$ -trimethylpimelate, b.p. 160—190°/10 mm. This is hydrolysed, decarboxylated, and esterified to *Et* γ -carbethoxy- $\alpha\beta\beta$ -trimethylpimelate (I), b.p. 118—122°/14 mm., which is hydrolysed (KOH-EtOH) to the acid, m.p. 61—62°. (I) with mol. Na in xylene at room temp. and then at 120—130° is cyclised to a product which could not be distilled but is hydrolysed and decarboxylated to a pasty acid from which, after esterification, *Et* 2:2:3-trimethylcyclohexan-4-onecarboxylate, b.p. 115—119°/7 mm., is obtained; the acid, m.p. 69—70°, derived therefrom is identical with Manasse's CO-acid.
H. W.

Difference in odour of *d*-, *l*-, and *dl*-derivatives of amino- and bisamino-methylenecamphors. B. K. SINGH and A. B. LAL (Nature, 1939, **144**, 910—911).—The order of intensity of odour in the isomerides of 5- and 3-nitro-*o*-toluidino-2:5- and -2:3-tolylenebisaminomethylenecamphor is $l > dl > d$. The 3- NO_2 - have a stronger odour than the 5- NO_2 -compounds.
L. S. T.

Addition reactions to conjugated systems. II. Caryophyllene and maleic anhydride. N. F. GOODWAY and T. F. WEST (J.C.S., 1939, 1853—1855).—Contrary to the indication of the tests proposed by Sandermann and by Fieser, the absorption spectrum of the mixture of sesquiterpenes known as caryophyllene shows the absence of any appreciable quantity of a conjugated isomeride. The caryophyllene-maleic anhydride adduct with MeOH-HCl gives a Me_2 ester, b.p. 180—183°/3 mm., and not a monoalkyl lactonic ester of the type derived from the normal adducts of α -phellandrene and dicyclohexenyl. This result throws doubt on the suggestion put forward by Rydon (A., 1939, II, 272).
F. R. S.

Constituents of *Didymocarpus pedicellata*. III. Isolation of a sesquiterpene and two polyterpene products and examination of the fatty matter. S. WARI and S. SIDDIQUI (J. Indian Chem. Soc., 1939, **16**, 423—426).—The essential oil fraction from *D. pedicellata* (A., 1938, II, 196) yields *didymocarpene*, b.p. 136—137°/3 mm., 147—148°/12 mm., $[\alpha]_D^{20} -3.7^\circ$ in 1% EtOH (nitrosobisnitrosite, m.p. 132—134°), a doubly unsaturated sesquiterpene. The heavier essential oil and non-volatile fatty residue contains *didymocarpol*, $(C_{10}H_{20}O)_5$, m.p. 76°, a saturated polyterpene, and *didymocarpenol*, $C_{25}H_{42}O$, m.p. 137°. The saturated acids formed by saponification are palmitic, behenic, lignoceric, and stearic (I). Free (I) is present in pedicin leaves.
F. R. G.

O-Acetyl derivative, m.p. 282—284° (decomp.), of quinovic acid.—See A., 1940, III, 83.

Preparation and reactions of karanjin. N. V. S. RAO, J. VEERABHADRARAO, and T. D. SESHADRI (Proc. Indian Acad. Sci., 1939, **10**, A, 65—70).—Treatment of the oil from the seeds of *Pongamia glabra* with $H_2SO_4-H_2O$ (2:1) gives K_2SO_4 .

Extraction of the oil with hot EtOH (apparatus described) affords karanjin (I), m.p. 158—159°, in 0.9% yield. Hydrolysis of (I) by EtOH-KOH gives mainly *C*-acetylkaranjol with a little karanjic acid (II). Molten KOH causes extensive decomp. and only BzOH can be isolated. KOH in H₂O-EtOH (3 : 2) gives a good yield of (II) with a little BzOH. (I) is slowly transformed by Hg(OAc)₂ in boiling, anhyd. MeOH into diacetoxymercurikaranjin. H. W.

Chemistry of *Aesculus* saponin and its structure. E. BUREŠ and F. VOLÁK (Časop. Českoslov. Lék., 1937, 17, 21—27, 41—50).—The saponin (I) obtained by pptn. with Et₂O or freezing from an EtOH extract of the seeds of the chestnut has a non-sugar-like basic structure, common to all the *Aesculus* saponins, the m.p. of which lie between the limits 174—206°. Attempted acetylation gives a hydrolysis product forming an osazone, m.p. 128—129°. The prosapogenin (II) is obtained by hydrolysing (I) as rhombic crystals, m.p. 228°, but cannot be assumed to be a chemical individual as its prep. cannot be repeated. Heating (I) or (II) for 100 hr. in 6% H₂SO₄-EtOH gives æscigenin (III) separated as its K salt and forming an OAc-derivative, C₃₅H₅₄O₃(OAc)₄, and phenylhydrazone, C₃₅H₅₈O₄(N-NHPh)₃. (III) is therefore C₃₅H₅₄(CO)₃(OH)₄, mol. wt. 590.46 (cryoscopic val. 612). F. R.

Specificity and relationship between chemical structure and vitamin-E activity.—See A., 1940, III, 54.

Action of magnesium alkyl halides on coumarin and related compounds. Synthesis of 2 : 2-dialkyl-1 : 2-benzopyrans. R. L. SHRINER and A. G. SHARP (J. Org. Chem., 1939, 4, 575—582).—A series of 2 : 2-dialkyl-1 : 2-benzopyrans has been prepared by the action of Mg alkyl halides on coumarin (I). The structure of these compounds has been demonstrated by means of their physical consts., ozonolysis to *o*-OH·C₆H₄·CHO, and hydrogenation to 2 : 2-dimethylchroman. Evidence is adduced in favour of the view that formation of these 2 : 2-dialkyl-1 : 2-benzopyrans probably involves the production of an intermediate co-ordination compound in which the alkyl group undergoes an $\alpha\gamma$ shift. Subsequent reaction with a second mol. of the Grignard reagent produces the dialkylbenzopyran. Gradual addition of an Et₂O solution of (I) to the Mg alkyl halide in Et₂O gives the following 2 : 2-dialkyl-1 : 2-benzopyrans : Me₂ (II), b.p. 79—80°/2.5 mm.; Et₂, b.p. 99—100°/2.8 mm.; Prⁿ, b.p. 118—120°/2.8 mm.; Buⁿ, b.p. 138—140°/2.8 mm.; di-*n*-amyl-, b.p. 156—158°/3 mm.; di-*n*-hexyl-, b.p. 174—176°/3 mm.; di-*n*-heptyl-, b.p. 192—193°/3 mm. A clear solution of (II) turns red when kept, reduces KMnO₄, decolorises Br, and is stable towards EtOH-alkali. Cold conc. H₂SO₄ gives a dark red colour and causes polymerisation, also caused by FeCl₃ in solution in Et₂O or AcOH saturated with HCl. Boiling AcOH does not cause isomerisation.

o-OH·C₆H₄·CH·CHAc and MgMeI yield δ -*o*-hydroxy-phenylpentan- β -one, m.p. 127—129° (decomp.) (semicarbazone, m.p. 155—155.5°), which passes at its m.p. into 2 : 4-dimethyl-1 : 2-benzopyran, b.p. 79—80°/3

mm.; this is ozonised in CCl₄ and then converted by Zn dust and H₂O into *o*-OH·C₆H₄·COMe. Interaction of *trans*-*o*-hydroxycinnamic acid with MgMeI leads to *o*-OH·C₆H₄·CH·CHAc. H. W.

Synthesis of coumarins from *o*-hydroxyaryl alkyl ketones. II. Formation of *o*-coumaric acids from *o*-hydroxyaldehydes. D. CHAKRAVARTI and B. MAJUMDAR (J. Indian Chem. Soc., 1939, 16, 389—392; cf. A., 1938, II, 334).—*o*-OMe·C₆H₄·CHO or 2 : 4 : 1-(OMe)₂C₆H₃·CHO and CH₂Br·CO₂Et (I)-Zn-C₆H₆ at 100° (bath) give Et β -hydroxy- β -2-methoxy-, b.p. 150—154°/10 mm., or 2 : 4-dimethoxyphenylpropionate, b.p. 180—184°/8 mm., respectively, dehydrated by SOCl₂-C₅H₅N-Et₂O to *Et* 2-methoxy-*trans*-cinnamate, b.p. 150°/8 mm., or Et 2 : 4-dimethoxy-*trans*-cinnamate, b.p. 180—184°/8 mm., which with KOH-EtOH give 2-methoxy-, m.p. 182° (identical with that from *o*-coumaric acid by methylation and hydrolysis), or 2 : 4-dimethoxy-*trans*-cinnamic acid, m.p. 184°, respectively. The *trans*-esters do not form coumarins. *o*-OMe·C₆H₄·CHO and Zn-CHBrMe·CO₂Et (II) afford Et β -hydroxy- β -2-methoxyphenylisobutyrate, b.p. 155°/4 mm., and thence Et *trans*-2-methoxy- α -methylcinnamate, b.p. 150—155°/4 mm., and the *trans*-acid, m.p. 102°. (I) and 2 : 5 : 1-OMe·C₆H₃Cl·CHO give Et β -hydroxy- β -5-chloro-2-methoxyphenylpropionate, b.p. 185°/4 mm., dehydrated to *Et trans*-5-chloro-2-methoxy-*cinnamate*, b.p. 170°/6 mm., which gives the *trans*-acid, m.p. 191°, also obtained from 5-chloro-*o*-coumaric acid. 1 : 2 : 4-C₆H₃Ac(OMe)₂ (III) and (II)-Zn, after vac. distillation, give Et 2 : 4-dimethoxy- $\alpha\beta$ -dimethylcinnamate, b.p. 180—182°/6 mm., converted by H₂SO₄ in the cold or by HI (*d* 1.7) at 140° into 7-methoxy- or -hydroxy-3 : 4-dimethylcoumarin, respectively. (I) and (III)-Zn give Et 2 : 4-dimethoxy- β -methylcinnamate, b.p. 174°/6 mm., but ring-closure was not effected. A. T. P.

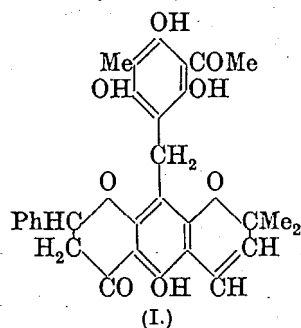
Synthesis of 5-hydroxy-8-methoxyflavone (primetin monomethyl ether). W. BAKER, N. C. BROWN, and (in part) J. A. SCOTT (J.C.S., 1939, 1922—1927).—2 : 6-(OH)₂C₆H₃·COMe is oxidised (K₂S₂O₈) to the 2 : 3 : 6-(OH)₃-compound, decomp. >230° (Ac₃ derivative, m.p. 155°), and with CH₂PhCl in COMe₂ gives a mixture of 2-hydroxy-6-benzylloxy- (I), m.p. 109—110°, and 2 : 6-dibenzylloxy-acetophenone, m.p. 71.5°. Oxidation of (I) with K₂S₂O₈ affords 2 : 5-dihydroxy-6-benzylloxyacetophenone, m.p. 94°, which is methylated (Me₂SO₄) to the 2 : 5-(OMe)₂-compound, m.p. 74°, debenzylated to 2-hydroxy-3 : 6-dimethoxyacetophenone, m.p. 61°. This compound is benzoylated to the 2-*O*-CH₂Ph-derivative, m.p. 119°, which with NaNH₂-PhMe yields 2-hydroxy-3 : 6-dimethoxydibenzoylmethane, m.p. 165°, cyclised (NaOAc-AcOH) to 5 : 8-dimethoxyflavone, m.p. 144—145°; this is demethylated with AlCl₃ in Et₂O to 5-hydroxy-8-methoxyflavone (primetin Me ether), m.p. 209—210°, identical with a natural specimen, further confirmed by the identity of the Ac derivative, m.p. 175—176°. Further demethylation to primetin has not been accomplished.

Attempts have been made to synthesise 6 : 8-dihydroxyflavone. Oxidation (K₂S₂O₈) of 2-hydroxy-3-methoxyacetophenone gives 2 : 5-dihydroxy-3-

methoxyacetophenone, m.p. 172° (Ac_2 derivative, m.p. 127°), in poor yield. 2:5-(OH)(OMe) C_6H_3 ·COMe is oxidised ($K_2S_2O_8$) to a mixture of 2:3-dihydroxy-5-methoxyacetophenone (II), m.p. 120°, and 2:2'-dihydroxy-5:5'-dimethoxy-3:3'-diacetyldiphenyl, m.p. 202°. The Me derivative of (II) with BzCl affords 2-benzoyloxy-3:5-dimethoxyacetophenone, m.p. 142°, which with $NaNH_2$ -PhMe is not converted into the dibenzoylmethane. *o*-Vanillin is oxidised ($K_2S_2O_8$) to a mixture of 4:4'-dihydroxy-3:3'-dimethoxydiphenyl-5:5'-dialdehyde, m.p. 210°, and 2:5-dihydroxy-3-methoxybenzaldehyde, m.p. 143°, which is methylated (Me_2SO_4) to the 2:3:5-(OMe) $_3$ -derivative, m.p. 63° (lit. 71°). Oxidation ($KMnO_4$) and esterification of the aldehyde gives Me 2:3:5-trimethoxybenzoate, b.p. 178—180°/20 mm., which with COMePh-Na yields 2:3:5-trimethoxydibenzoylmethane, m.p. 82°, which has not been cyclised.

F. R. S.

Rottlerin. II. H. BROCKMANN and K. MAIER (Annalen, 1939, 541, 53—75).—A more detailed account of work previously reviewed (A., 1939, II, 334). *iso*Rottlerin (I) (improved prep.; cf. A., 1938, II, 334) is isomerised by treatment with K_2CO_3 in COMe $_2$ (and acidification of the resulting solution) to ψ -rottlerin (II), m.p. 193—194° [penta-acetate, m.p. 176—177.5° (previous sintering)], which resembles rottlerin, is reconverted by boiling AcOH into (I), and [unlike (I)] gives PhCHO with boiling $2N$ -NaOH. Reactions indicate that (II) is the enolic form of (I). Dihydroisorttlerin (III) and dihydro- ψ -rottlerin (IV), m.p. 206—207° or 215—216° (penta-acetate, m.p. 181—182.5°), are similarly interconvertible. Reduction (H_2 , Pd-black, COMe $_2$) of (II), (IV), or (I) (in presence of K_2CO_3) gives tetrahydro- ψ -rottlerin (V), m.p. 225—226°, also obtained in smaller yield from (III) (using PtO_2); (V) is sometimes obtained from (I) in absence of K_2CO_3 . The compounds, m.p. 209° and 225—228°, of Bakshi *et al.* (A., 1939, II, 275) are probably (III) and (V), respectively. Methylation of (I) with Me_2SO_4 in COMe $_2$ + K_2CO_3 affords ψ -rottlerin Me $_5$ ether (VI), m.p. 135—136° (cf. Narang *et al.*, A., 1938, II, 66), reduced (H_2 , Pd-black, C_5H_5N , COMe $_2$) to a H_2 -derivative (VII), m.p. 123—124°. An isomeric dihydro- ψ -rottlerin Me $_5$ ether (VIII), m.p. 134°, is obtained by methylation [as for (I)] of (III). Tetrahydro- ψ -rottlerin Me $_5$ ether, m.p. 98°, is formed (with some Me $_4$ ether, m.p. 154—156°) by methylation of (V) and (solely) reduction (Pd) of (VI), (VII), or (VIII). Rottlerin Me $_5$ ether is reduced to its H_2 -derivative, m.p. 86—87°, which does not give PhCHO when ozonised [(II), (IV), (VI), and (VIII) similarly afford 0.58, 0.79, 0.76, and 0.88 mol. of PhCHO, respectively]. Prolonged interaction of diazoaminobenzene and (II) in COMe $_2$ gives (?) benzeneazo- ψ -rottlerin, decomp. from 265°, and the same benzeneazomethylphloracetophenone (IX) as is obtained from rottlerin; (IX) is similarly produced from (IV),



(V), and tetrahydrorottlerin. Tetrahydro- ψ -rottlerinone, (?) $C_{21}H_{24}O_4$, m.p. 179° (sinters 170—171°) [from (V) and $2N$ -NaOH at <65°], is methylated (Me_2SO_4 - K_2CO_3 -COMe $_2$) to a Me $_2$ ether, m.p. 87—89°. Absorption spectra of many of the above compounds are given.

H. B.

Rottlerin. IV. Derivatives of isorttlerin. R. S. JALOTA, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1939, 16, 405—409; cf. A., 1938, II, 108, 455).—*iso*Rottlerin (I) (cf. Brockmann *et al.*, A., 1938, II, 334) is identical with the colouring matter, m.p. 181° (*ibid.*, 66). Separation of rottlerin (II) and (I) is best effected chromatographically. (II) and 90% aq. EtOH-HCl (d 1.15) give (I). (I) and Me_2SO_4 - $KHCO_3$ -COMe $_2$ at 100° (bath) give isorttlerin Me $_4$ or Me $_5$ ether (III), new m.p. 135—138° [piperonylidene derivative, m.p. 147°; $NaNO_2$ -AcOH at 30° give the nitrosite, m.p. 194—197° (decomp.), unchanged on attempted catalytic reduction, and on heating alone or with alkali gives PhCHO], oxidised by 30% H_2O_2 -MeOH-aq. NaOH at 50° to the ether oxide, m.p. 120—122°, which when heated at > m.p. gives PhCHO. Reduction of (I) (Adams' PtO_2 -EtOAc or Pd-C) gives dihydroisorttlerin (IV), m.p. 209°; similarly, once cryst. (I) gives (IV) and a substance, (?) $C_{22}H_{24}O_8$, m.p. 225—228°. (III), or the Me ether of (IV), and Zn-AcOH afford a substance, m.p. 162—164°. Rottlerin Me $_5$ ether similarly gives a substance, m.p. 184° (softens from 179°), unchanged on attempted reduction (Adams' catalyst), or acetylation (Ac_2O - C_5H_5N), or oxidation (alkaline H_2O_2). The constitution of (II) suggested by Brockmann *et al.* (*loc. cit.*) or McGookin *et al.* (A., 1938, II, 199) is doubted.

A. T. P.

Thiophen series. XLIX. Constitution of indophenines. W. STEINKOPF and W. HANSKE (Annalen, 1939, 541, 238—260).— α -Indophenines, *i.e.*, those derived from thiophens with free H at positions 2 and 5, are proved to have structures of type (A) (cf. Schlenk *et al.*, A., 1923, i, 1235). Mg 2-thienyl iodide (I) and isatin in C_6H_6 give 3-2'-thienyldioxindole, m.p. 208—208.5° (= (A) (blue melt) (ON-Bz $_2$ derivative, m.p. 159°), which with anhyd. ZnCl $_2$ at 180° affords isatin-thiophen-indophenine (A., 1932, 752). Et 5-bromo-3-2'-thienyldioxindole-1-acetate, m.p. 124—125° [from (I) and Et 5-bromoisatin-1-acetate in Et $_2O$], is converted by AcOH-conc. H_2SO_4 at 55—60°/10 min. into 5-bromo-1-carbethoxymethylisatin-thiophen-indophenine (*loc. cit.*); 5-bromo-3-2'-thienyl-, m.p. 217.5° (decomp.), and 3-2'-thienyl-1-methyldioxindole, m.p. 127.5—129° (blue melt), from (I) and 5-bromo- and 1-methyl-isatin, respectively, are similarly transformed into indophenines. The product, b.p. 146—151°/3 mm., from CO(CO $_2$ Et) $_2$ and (I) must contain $2-C_4H_5S\cdot C(OH)(CO_2Et)_2$ since short treatment with conc. H_2SO_4 gives mesoxophenine (II) [Et mesoxalate-thiophen-indophenine] (Schlenk, *loc. cit.*), which is hydrolysed (MeOH-KOH-dioxan) to glyoxylic acid-thiophen-indophenine (K_2 salt). Reduction (Zn dust, AcOH) of (II) affords Et $_4$ 2:2'-dithienyl-5:5'-di(malonate), m.p. 111.5—112.5°, hydrolysed (EtOH-KOH in absence of air) to 2:2'-di-

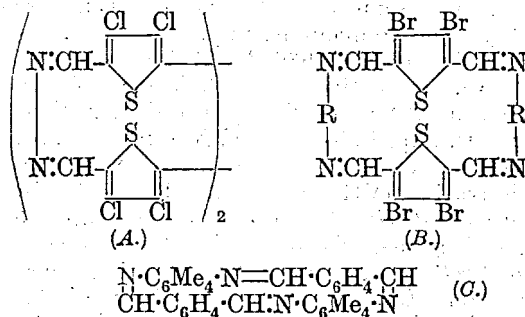
thienyl-5:5'-di(acetic acid), m.p. 217° (darkens at 210°) (Me_2 ester, m.p. 75.5–77°), which is decarboxylated (Cu powder in a vac.) to the known 5:5'-dimethyl-2:2'-dithienyl. Accordingly, (II) is *A* with $Ph = R = CO_2Et$. *Et* α -hydroxy- α -2'-thienylphenylacetate, b.p. 136°/0.3 mm., m.p. 59.5–60.5° [from (I) and $BzCO_2Et$], is converted by conc. H_2SO_4 (5 min. at room temp.) into *Et* phenylglyoxylate-thiophen-indophenine (III) (*A*, $R = CO_2Et$), m.p. 208° [corresponding acid (IV) (*A*, $R = CO_2H$), m.p. 208–210° (decomp.) (K_2 salt)], also obtained directly from $BzCO_2Et$, thiophen, and conc. H_2SO_4 in cold light petroleum. Reduction (Zn dust, AcOH) of (III) gives *Et* 2:2'-dithienyl-5:5'-di-(α -phenylacetate), m.p. 95–96.5°; the corresponding acid, m.p. 70–85° (decomp.) [from (IV), Zn dust, and aq. NH_3-NH_4Cl], loses CO_2 at 250° and affords 5:5'-dibenzyl-2:2'-dithienyl (V), m.p. 96.5–97.5°, which is also obtained when (IV) is heated in a vac. (? reduction of part of the mol. at the expense of another part). When a solution of (IV) in 2*N*- NH_3 is kept until the original red colour disappears, 5:5'-dibenzoyl-2:2'-dithienyl (VI), m.p. 250–252° (3:3'- Br_2 -derivative, m.p. 195–197°), separates; (VI) is synthesised from 2:2'-dithienyl, $BzCl$, and $TiCl_4$ in C_6H_6 . A possible intermediate in the production of (VI) from (IV) is the compound (*A*, $R = OH$). The Mg derivative from (I) and Bz_2 with $Et_2O-CH_2N_2 + aq. NH_4Cl$ gives *ms*-2'-thienylbenzoin *Me* ether, m.p. 71–72°, converted by AcOH–conc. H_2SO_4 at 45–50° into benzil-thiophen-indophenine (VII) (*A*, $R = Bz$), m.p. 223°; thiophen, Bz_2 , and conc. H_2SO_4 in cold $CHCl_3$ afford *ms*-di-2'-thienyldeoxybenzoin, m.p. 103.5–104°. Reduction (Zn dust, AcOH) of (VII) yields 5:5'-didesyl-2:2'-dithienyl, m.p. 219.5–220.5° (blue melt), which is cleaved by $EtOH-NaOEt$ in H_2 to (V) and $NaOBz$.

2-Benzyl- and 2:5-dibenzyl-thiophen, b.p. 220–222°/12 mm., are obtained from thiophen, CH_2Ph-OH , and $ZnCl_2$. 5-Iodo-2-benzylthiophen, m.p. 55–57° (from the 5- $ClHg$ -derivative and aq. $KI-I$ at 50°), and Cu powder at 185–210° in N_2 give (V). *ms*-2'-Thienylacetoin, b.p. 82°/1 mm. [from (I) and Ac_2], with conc. H_2SO_4 affords an unstable indophenine.

Isatin-thiophen-indophenine (*A*, with $:CPhR = :C \begin{smallmatrix} CO \\ \diagup \diagdown \\ C_6H_4 \end{smallmatrix} NH$), (VII), and 2:3-diketo-4:5-benzofuran-thiophen-indophenine (VIII), m.p. >300° (from components in AcOH–conc. H_2SO_4 at 55°), are all blue; compounds, e.g., (II), (III), (IV), derived from $RCO-CO_2R'$ are red or bluish-violet. Fission of (VIII) by alkali thus gives a red solution of the α -hydroxyphenylglyoxylic acid derivative. β -Indophenines, i.e., those from thiophenes with free H at positions 2 and 3, are now considered (cf. A., 1932, 752) to be of type (B). *ms*-5'-Methyl-2'-thienylbenzoin, m.p. 78–79° (from Mg 5-methyl-2-thienyl iodide and Bz_2), affords an unstable indophenine whilst *ms*-5'-bromo-2'-thienylbenzoin, m.p. 99.5–100.5° (violet melt), is converted into an indophenine with difficulty. 2-Iodo-3-thiotolen-5-carboxylic acid, m.p. 172–173°, is prepared (Grignard method) from the 2:5- I_2 -derivative.

H. B.

Thiophen series. L. Derivatives of 3:4-dibromothiophen-2:5-dialdehyde and macrocyclic compounds. W. STEINKOPF, R. LEITSMANN, A. H. MÜLLER, and H. WILHELM (Annalen, 1939, 541, 260–282; cf. A., 1938, II, 154).—Comparison of the colours of various derivatives of 3:4-dibromothiophen-2:5-dialdehyde (I) [*dianil*, m.p. 245° (rapid heating); *di*- α -hydroxyanil, m.p. 214° (decomp.); *di*- p -acetamidoanil, decomp. >300°] with those of p - $C_6H_4(CHO)_2$ (*dianil*, m.p. 159°; *di*- α -hydroxyanil, m.p. 215°; *di*- p -acetamidoanil, m.p. 320–322°) and (in some cases) m - $C_6H_4(CHO)_2$, shows that the conjugated double linkings of the thiophen ring exert a bathochromic effect (cf. A., 1937, II, 163). 2-Methylquinoline and (I) in boiling Ac_2O give 3:4-dibromo-2:5-di-(β -2'-quinolylvinyl)thiophen, m.p. 247–249° (*di*hydrochloride); *m*-, m.p. 180°, and *p*-, m.p. 243°, -di-(β -2'-quinolylvinyl)benzene are similarly prepared. 3:4-Dibromothiophen-2:5-di-acrylic acid, m.p. >350° [*chloride* (by $SOCl_2$), m.p. 172° (decomp.)], is obtained from (I), Ac_2O , and $NaOAc$ at 170–175°. 5:5'-Dimethyl-2:2'-dithienyl, m.p. 67° (prep. from 5-iodo-2-thiotolen and Cu powder), and Br in CS_2 give the 3:4:3':4'- Br_4 -derivative, m.p. 255°, which with Br at ~70° (irradiated in absence of moisture) affords 3:4:3':4'-tetrabromo-5:5'-di-(bromomethyl)-2:2'-dithienyl, m.p. 210°, in 11–15% yield; the 3:4:3':4'- Cl_4 -derivative, m.p. 201° (prep. with Cl_2 –AcOH), with Cl_2 in boiling CCl_4 and sunlight gives 3:4:3':4'-tetrachloro-5:5'-di-(dichloromethyl)-2:2'-dithienyl, m.p. 119–120°, which is converted by aq. $Ca(OH)_2 + CaCO_3$ into 3:4:3':4'-tetrachloro-2:2'-dithienyl-5:5'-dialdehyde, m.p. 179°. This affords [as for (I)] 3:4:3':4'-tetrachloro-5:5'-di-(β -2'-quinolylvinyl)-2:2'-dithienyl, m.p. 284°, and with $N_2H_4 \cdot H_2O$ in AcOH yields the dark red, insol., infusible azine (*A*). The following di-imines, m.p. >400° unless stated otherwise, are prepared from (I) or $C_6H_4(CHO)_2$ and the appropriate diamines: *bis*-(3:4-dibromo-2:5-thioxyldiene)-ethylenediamine (*B*, $R = [CH_2]_2$), *o*-phenylenediamine (*B*, $R = o$ - C_6H_4), decomp. 262° (sinters 230°) [accompanied by 3:4-dibromo-2:5-di-(2'-benziminazolyl)thiophen, m.p.



385°], *m*-phenylenediamine, -2:2'-diaminodiphenyl (*B*, $R = oo$ -diphenylene), viscous ~230° (softens ~220°), -benzidine (II) (*B*, $R = pp'$ -diphenylene), and -4:4'-diaminodiphenylmethane (*B*, $R = C_6H_4 \cdot CH_2 \cdot C_6H_4$); *bis*- p -xylylidene-ethylenediamine, -diaminodurene (*C*), and -4:4'-diaminodiphenylmethane; *bis*- m -xylylidene-diaminodurene and -benzidine. p - $C_6H_4(CHO)_2$ and o - $C_6H_4(NH_2)_2$ in AcOH give *p*-di-(2'-benziminazolyl)benzene, decomp. >300°. A little

3 : 4-dibromothiophen-2 : 5-dialdehydedi-*p-p'*-amino-phenylanil [3 : 4-dibromo-2 : 5-thioxylidenebisbenzidine] (III), m.p. $>450^\circ$, is formed with (II); (III) and (I) in EtOBz-AcOH afford (II).

NPhMe₂, (I), and ZnCl₂ at 110–120° give 3 : 4-dibromo-2 : 5-di-(*pp'*-tetramethyldiaminobenzhydryl)-thiophen, m.p. 246°, oxidised (MnO₂, dil. H₂SO₄) to the dicarbinol, m.p. ~ 180 –185° (previous sintering), which with EtOH-conc. H₂SO₄ in C₆H₆ affords the dye, C₃₈H₄₀N₄Br₂S(HSO₄)₂ [dibromothiophen-blue]. Similarly, *m*- and *p*-C₆H₄(CHO)₂ yield 1 : 3-, m.p. 147–149°, and 1 : 4-, m.p. 244–245° (decomp.), -di-(*pp'*-tetramethyldiaminobenzhydryl)benzenes, whence the dicarbinols, m.p. 135–140° (previous sintering) and 160–165°, respectively; the dyes, C₄₀H₄₄N₄(HSO₄)₂, give bluish-green solutions. 3 : 4 : 5-Tribromothiophen-2-aldehyde, NPhMe₂, and ZnCl₂ at 110–120° afford 3 : 4 : 5-tribromo-2-*pp'*-tetramethyldiaminobenzhydrylthiophen, m.p. 159–160°, whence tribromothiophen-green, C₂₁H₂₀N₂Br₃S(HSO₄)₂. H. B.

Preparation of 2 : 5-dimethylpyrrole from the corresponding monocarboxylic ester. N. M. TIMOSCHAYSKAJA (J. Gen. Chem. Russ., 1939, 9, 766).—2 : 5-Dimethylpyrrole is obtained (60–70% yield) by heating a mixture of Et 2 : 5-dimethylpyrrolecarboxylate with NaOH at 100–120°. Similarly 2 : 4-dimethylpyrrole (35% yield) is obtained from Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, and 1 : 2 : 5-trimethylpyrrole (20% yield) from Et 1 : 2 : 5-trimethylpyrrolecarboxylate. V. A. P.

Pyridine series. I, II. Synthesis of 2-methyl-4-ethylpyridine. I. R. H. SIDDIQUI. II. R. H. SIDDIQUI and A. Q. KHAN (J. Indian Chem. Soc., 1939, 16, 410–414, 415–418).—CH₃Ac·CO₂Et, EtCHO, and piperidine at 0°, then heated with NH₃ (*d* 0.88) at 100°, give Et₂ 2 : 6-dimethyl-4-ethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate (I), m.p. 112° (cf. Engelmann, A., 1886, 258), oxidised by NO₂ fumes in Et₂O (better) or I-EtOH to Et₂ 2 : 6-dimethyl-4-ethylpyridine-3 : 5-dicarboxylate, b.p. 135–140°/0.5 mm. (picrate, +H₂O, m.p. 116°). (I) and KOH-EtOH give the K salt, which on distillation with soda-lime gives 2 : 6-dimethyl-4-ethylpyridine (hydrochloride, m.p. 97°; picrate, new m.p. 121°), which with PhCHO-ZnCl₂ at 140°, then 180–185° [Ac₂O in place of ZnCl₂ gives (II) + (III) only], gives 2 : 6-distyryl-4-ethylpyridine (II), m.p. 85° [hydrochloride, m.p. 271–272° (decomp.)]; platinichloride, m.p. 263° (decomp.); aurichloride, m.p. 200°; picrate, m.p. 255°; and 2-styryl-6-methyl-4-ethylpyridine (III), b.p. 205°/2 mm. [hydrochloride, m.p. 208°; hydriodide, m.p. 203°; platinichloride, m.p. 243°; aurichloride, m.p. 145°; picrate, m.p. 232–233° (sublimes at 90° in vac.)], and (?) α -phenyl- β -6-(2-methyl-4-ethyl)pyridylethyl alcohol [hydrochloride, m.p. 175°; platinichloride, m.p. 125° (softens at 85°); picrate]. (II) is unchanged with PhCHO-Ac₂O at 100° (bath). (III) and KMnO₄-COMe₂ give BzOH and 6-methyl-4-ethylpyridine-2-carboxylic acid, decarboxylated (trace of Cu) to 2-methyl-4-ethylpyridine (picrate, +0.5H₂O, m.p. 142°). A. T. P.

Long-chain alkyl derivatives of 2-aminopyridine. T. M. SHARP (J.C.S., 1939, 1855–1857).—

2-Aminopyridine and the alkyl halide (10–14 C) in boiling cymene give a mixture of 1-alkyl derivatives of 2-pyridoneimine, strong, unstable bases formed in greater proportion, and 2-alkylaminopyridines, weaker, stable bases. The following are described: 2-decylaminopyridine, m.p. 51–52°; 1-decyl-2-pyridoneimine sulphate, m.p. 246° (decomp.); 2-undecylaminopyridine, m.p. 60–61°; 1-undecyl-2-pyridoneimine oxalate, efferv. 205°; 2-dodecylaminopyridine, m.p. 60°; 1-dodecyl-2-pyridoneimine sulphate, m.p. 255° (decomp.); 2-tridecylaminopyridine, m.p. 65–66°; 1-tridecyl-2-pyridoneimine sulphate, m.p. $\sim 265^\circ$; 2-tetradecylaminopyridine, m.p. 69°; 1-tetradecyl-2-pyridoneimine sulphate, m.p. $\sim 260^\circ$ (this substance obtained alone in presence of NaNH₂); and 1-benzyl-2-pyridoneimine sulphate, m.p. 261° (decomp.). Deamination of the corresponding imine affords 1-dodecyl-2-pyridone picrate, m.p. 96–97°.

F. R. S.

Salts of 2 : 6-diaminopyridine.—See B., 1940, 87.

Transformation of indolyl methyl ketones into indole homologues. II. C. ALBERTI (Gazzetta, 1939, 69, 568–583; cf. A., 1937, II, 387).—3-Methyl-2-indolyl Me ketone (I) and NaOMe or NaOEt at 210–220° give an amorphous product. With N₂H₄·H₂O in boiling EtOH, 3-indolyl Me ketone (II) gives its ketazine (III), m.p. 280–282° (decomp.). Under similar conditions, 2-methyl-3-indolyl Me ketone (IV) gives its ketazine (V), m.p. 263–265°. (I) gives its hydrazone (VI), m.p. 142–144°, with the ketazine (VII), m.p. 234–236°, into which (VI) is converted when heated, or treated with I in EtOH. With NaOMe-EtOH at 180–200°, (III) gives 3-ethylindole (VIII), with a compound (IX), C₁₀H₁₁N₃ or C₁₀H₁₃N₃, m.p. 120–121°. With N₂H₄·H₂O-EtOH at 100°, followed by NaOEt-EtOH at 180–200°, (II) gives (VIII) and (IX). At 180–200°, (V) [or (IV) and N₂H₄·H₂O] and NaOEt-EtOH give 2-methyl-3-ethylindole, and a compound, C₁₁H₁₃N₃, m.p. 162–163°. With NaOEt-EtOH at 170–180°, (VI) or (VII) [or (I) and N₂H₄·H₂O] gives 3-methyl-2-ethylindole. E. W. W.

Synthesis of nitrogen ring compounds. XVIII. 4th Group. Synthesis of condensed nitrogen ring systems. III. Synthesis of octahydropyridocoline. S. SUGASAWA and N. LEE (J. Pharm. Soc. Japan, 1939, 59, 113–115).—Catalytic reduction of Et γ -2-pyridylbutyrate yields Et γ -2-piperidylbutyrate, b.p. 114°/4 mm., converted at 200° into 4-keto-octahydropyridocoline, b.p. 118°/0.3 mm., which with K₂S and P₂S₅ in xylene yields 4-thioketo-octahydropyridocoline, b.p. 162°/0.3 mm., m.p. 162°. Reduction of this in EtOH at a Pb cathode yields octahydropyridocoline. J. D. R.

Compounds of iodine trichloride with pyridine, quinoline, and trimethylamine. E. V. ZAPPI and M. FERNANDEZ (Anal. Asoc. Quim. Argentina, 1939, 27, 102–126).—The compounds formed by bases with ICl₃, ICl₂, and I are readily interconverted. The following are new: C₅H₅N·ICl₃, m.p. 195–196° (decomp.), prepared by the anhyd. addition of ICl₃ to C₅H₅N or Cl₂ to C₅H₅N·I₂ or C₅H₅N·ICl; C₉H₇N·ICl₃, m.p. 152–160° (decomp.) [hydrochloride, m.p. 185°

(decomp.); $NMe_3 \cdot ICl_3$, m.p. 177° (decomp.). A reaction with NEt_3 could not be established nor could compounds with ICl_2 be prepared. F. R. G.

Transformations of *Bz*-hydroxyquinoline derivatives. II. I. M. KOGAN and T. A. SOSNOSKI (J. Appl. Chem. Russ., 1939, 12, 1147—1153; cf. A., 1931, 1306).—Diazotisation of 5-amino-6-hydroxyquinoline-8-sulphonic acid (I) yields 5-diazo-6-hydroxyquinoline-8-sulphonic acid (II) (NH_4 salt; compounds with β - $C_{10}H_7 \cdot OH$ and with $Ac \cdot [CH_2]_2 \cdot CO_2Et$), reduced by $SnCl_2$ to 5-hydrazino-6-hydroxyquinoline-8-sulphonic acid. (I) and 20% HNO_3 at 50° yield (II).

R. T.

Complexes of polynitro-compounds. III. **Compounds of polynitro-substances with derivatives of carbostyryl etc.** A. KENT, D. McNEIL, and R. M. COWPER (J.C.S., 1939, 1858—1862).— Me , derivatives of carbostyryl and of $NPh(CH_2Ph)_2$ and some other derivatives of the former have been examined with reference to their capacity to afford cryst., termol. (1:2) compounds. Some exceptions have been observed, including a cryst. 2:3 product from $s\text{-}C_6H_3(NO_2)_3$ (X) and dibenzyl-*m*-toluidine but 13 substances afford 16 new examples of ternary complexes with X or with picric acid (Y). The Y compounds prepared include some "salt-like" types with carbostyryls and with 2-quinolones for which a "H-bond" is suggested. The following compounds are described: carbostyryl, XA_2 , m.p. 178° , and AY , m.p. 132° ; thiocarbostyryl, XA' , m.p. 163 — 165° , and YA' , m.p. 145° ; dihydrocarbostyryl, XB_2 , m.p. 137 — 138° ; 3-methylcarbostyryl, XC_2 , m.p. incongruent, and YC_2 , m.p. incongruent; 4-methylcarbostyryl, XD_2 , m.p. 226 — 227° , and DY , m.p. 164 — 165° ; 4-methyl-2-thiocarbostyryl, XD'_2 , m.p. 190 — 192° , and YD'_2 , m.p. 193 — 195° ; 5-methylcarbostyryl, XE_2 , m.p. 222 — 223° , and EY , m.p. 156 — 157° ; 6-methylcarbostyryl, FY , m.p. 171 — 172° ; 6-methyl-2-thiocarbostyryl, XF'_2 , m.p. 159 — 161° , and compound with Y (?), m.p. 140 — 142° ; 7-methylcarbostyryl, YG_2 , m.p. 203 — 204° , and GY , m.p. 163° ; 8-methylcarbostyryl, XH_2 , m.p. 181° , and HY , m.p. 128 — 129° ; 4:6-dimethylcarbostyryl, XL_2 , m.p. incongruent, and LY , m.p. 188° ; 4:7-dimethylcarbostyryl, XM_2 , m.p. 213 — 214° , and MY , m.p. 189 — 191° ; 4:8-dimethylcarbostyryl, XN_2 , m.p. 199 — 200° , and NY , m.p. 192 — 194° ; 1-methyl-2-quinolone, XP , m.p. 77 — 79° , and PY , m.p. 128 — 129° ; 1-methyl-2-thioquinolone, XP'_2 , m.p. 98 — 99° , and YP'_2 , m.p. 104° ; 1:6-dimethyl-2-quinolone, QY , m.p. 150° ; 1:7-dimethyl-2-quinolone, XR , m.p. 106 — 107° , and RY , m.p. 132° ; 1:8-dimethyl-2-quinolone, SY , m.p. 134° ; 2-methoxyquinoline, XV , m.p. 89 — 90° , and UY , m.p. 170 — 171° ; 2-methylthioquinoline, XU' , m.p. 99 — 100° , and $U'Y$, m.p. 183 — 184° ; 2-methoxy-6-methylquinoline, XV' , m.p. 72 — 73° , and VY , m.p. 181 — 182° ; 2-methylthio-6-methylquinoline picrate, m.p. 196 — 197° ; 2-methylthio-1-methylquinolinium picrate, m.p. 175° ; 2-chloro-7-methylquinoline, m.p. 81° (picrate, m.p. 113 — 114°); 3-methylquinoline oxide hydrochloride, m.p. 192 — 194° (picrate, m.p. incongruent); 6-methylquinoline oxide hydrochloride, m.p. 172 — 173° (picrate, m.p. 174 — 175°); 5-, m.p. 222 — 223° , and 7-methylcarbo-

styryl, m.p. 192 — 193° ; 1:7-dimethyl-2-quinolone, m.p. 107 — 108° ; 1:6-dimethyl-2-thioquinolone, m.p. 137° ; dibenzyl-*o*-toluidine picrate, m.p. 120 — 121° ; $m\text{-}C_6H_4Me \cdot N(CH_2Ph)_2 + X$ (3:2), m.p. 71 — 72° ; dibenzyl-*m*-toluidine picrate, m.p. 126 — 127° ; $p\text{-}C_6H_4Me \cdot N(CH_2Ph)_2 + X$, m.p. 62 — 64° ; dibenzyl-*p*-toluidine picrate, m.p. 174 — 175° ; 1-thiocoumarin picrate, m.p. 148° ; *trans*-*o*-aminocinnamic acid + X complex, m.p. 131° ; 2-thiocoumarin + X complex, m.p. 87° ; and 1:2:4:5- $C_6H_2Me(NO_2)_3$ and $CH_2(C_6H_4 \cdot NH_2 \cdot p)_2$ complex, m.p. 92 — 93° . F. R. S.

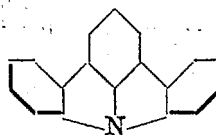
Quinoline derivatives. IV. (SIGNA.) L. MONTI and (SIGNA.) G. FERRARI DI CAPORCIANO (Gazzetta, 1939, 69, 745—749).—2-Hydroxy-6-methoxy-4-methylquinoline (A., 1932, 402) in $AcOH$ with nitrous fumes gives its 5- NO_2 , m.p. 278 — 280° (decomp.; sinters 260°), reduced ($FeSO_4 \cdot NH_3$, or, better, $Zn \cdot AcOH$) to the 5- NH_2 -derivative, m.p. 270 — 272° (hydrochloride, m.p. 240 — 242° ; picrate, m.p. 198 — 200° ; Ac derivative, m.p. 260 — 262° ; *p*-dimethylaminobenzylidene derivative, m.p. 260 — 262° ; 2-quinolymethylene derivative, decomp. 220 — 222°). E. W. W.

Derivatives of 3-nitro-4-hydroxyquinoline. II. **Synthesis of 3-nitro-4:6-dihydroxyquinoline.** M. COLONNA (Gazzetta, 1939, 69, 684—688).—2:5:1- $NH_2 \cdot C_6H_3(OH) \cdot CO_2H$ in conc. HCl with $KO \cdot N \cdot CH \cdot CH_2 \cdot NO_2$ gives 2- β -nitroethylideneamino-5-hydroxybenzoic acid, m.p. 218° (decomp.), which with boiling $KOAc \cdot Ac_2O$ yields 3-nitro-4:6-dihydroxyquinoline, decomp. $\sim 320^\circ$ (darkening from 280°) (Me_2 ether, m.p. 254°), reduced by $Sn \cdot HCl$ to the 3- NH_2 -compound, m.p. 312 — 313° (decomp.; darkens $\sim 300^\circ$), of which the Ac derivative (darkens $\sim 300^\circ$) with $EtI \cdot K_2CO_3 \cdot EtOH$ gives 3-acetamido-4:6-diethoxyquinoline, m.p. $\sim 100^\circ$ (from H_2O), 175° (anhyd.). E. W. W.

Action of chlorine on carbazole. J. S. SALKIND and M. E. MOMARENKO (J. Appl. Chem. Russ., 1939, 12, 1134—1136).—Carbazole in CCl_4 and Cl_2 yield tetrachloro-, m.p. 223 — 224° , and octachloro-carbazole.

R. T.

Attempts to prepare optically active tervalent nitrogen compounds. I. **Syntheses of 1:9-phenylenecarbazole and derivatives.** (Miss) H. G. DUNLOP and S. H. TUCKER (J.C.S., 1939, 1945—1956).—The theory is put forward that, in 1:9-phenylenecarbazole and its derivatives, if the whole mol. is planar, the N bonds are strained, but that this condition is partly relieved if the N adopts a position outside the plane of the C_6 rings. In such a structure the replacement by any atom or group of any H, other than that attached to the central C_6 nucleus, and *p* to the N, will give rise to an asymmetric mol., the asymmetry of which is conditioned by the non-planar orientation of the N^{III} bonds.



9-(2'-Nitrophenyl)carbazole (improved yield) is reduced ($SnCl_2 \cdot HCl \cdot AcOH$) to the 9-2'- NH_2 -compound, m.p. 119 — 121° , which is deaminated ($NaNO_2 \cdot H_2SO_4 \cdot AcOH$) to 1:9-phenylene-carbazole (I), m.p. 136.5 — 138.5° (picrate, m.p. 165 — 169° ; $s\text{-}C_6H_3(NO_2)_3$ compound, m.p. 192 — 194°). 9-Phenylcarbazole, m.p. 91 — 93° , prepared

from carbazole (II), PhI , and $\text{K}_2\text{CO}_3\text{-Cu}$, forms a *picrate*, m.p. 126—129°, and $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 132—134°. Similar condensation with (II) and 4-chloro-3-nitrotoluene gives 9-(2'-nitro-4'-methylphenyl)carbazole, m.p. 104—106°, reduced to the 2'- NH_2 -compound, m.p. 117—119°, which is deaminated to 1:9-(4'-methylphenylene)carbazole, m.p. 109—111° [*picrate*, m.p. 145—150°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 170—172°]. 9-Tolylcarbazole, m.p. 105—107°, forms a $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 106—108°. 9-(4'-Chloro-2'-nitrophenyl)carbazole, m.p. 134—136°, similarly prepared, is reduced to the NH_2 -compound, m.p. 84—86°, which could not be converted into the corresponding phenylenecarbazole. Reduction of 9-(2'-nitro-4'-aminophenyl)carbazole with $\text{Na}_2\text{S-EtOH}$ affords the 9-2'-nitro-4'-amino-compound, m.p. 164—166° (*Ac* derivative, m.p. 261—263°), and with $\text{SnCl}_2\text{-HCl-AcOH}$, the 2':4'-(NH_2)₂-compound, m.p. 128—130° (*Ac* derivative, m.p. 230—235°; 4'-*Ac* derivative, m.p. 235—245°), is obtained; these substances could not be cyclised. Condensation of (II) with 4-chloro-, 4-bromo-, or 4-iodo-3-nitroacetophenone, m.p. 112—115°, does not take place. 4-Chloro-3-nitrobenzonitrile and (II) condense to 9-(2'-nitro-4'-cyanophenyl)carbazole, m.p. 172—174°, reduced to the 2'- NH_2 -compound, m.p. 186—188°, cyclised and hydrolysed to 1:9-phenylenecarbazole-4'-carboxylic acid, m.p. 340°, in quantity insufficient for its resolution. $p\text{-C}_6\text{H}_4\text{I-CO}_2\text{Et}$ and (II) yield *Et* 9-phenylcarbazole-4-carboxylate, m.p. 97—100°, hydrolysed to the acid, m.p. 215—219°. PhCl , (II), and $\text{CCl}_3\text{-CN}$ give 3-trichloroacetylcarbazole, m.p. 206—208° (*Ac* derivative, m.p. 120—125°), hydrolysed to carbazole-3-carboxylic acid. The *Et* ester of this acid and $o\text{-C}_6\text{H}_4\text{Cl-NO}_2$ afford *Et* 9-(2'-nitrophenyl)carbazole-3-carboxylate, m.p. 120—122°, reduced to the 2'- NH_2 -compound, m.p. 140—142°, which is cyclised and hydrolysed to 1:9-phenylenecarbazole-3-carboxylic acid, m.p. 305°, a symmetrical substance. PhCl , (II), and $\text{CCl}_3\text{-CN}$ with AlCl_3 give carbazole-3:6-dicarboxylic acid, m.p. >360°, the *Et* ester of which with $o\text{-C}_6\text{H}_4\text{Cl-NO}_2$ yields *Et* 9-(2-nitrophenyl)carbazole-3:6-dicarboxylate, m.p. 202—203°, reduced to the 2- NH_2 -compound, m.p. 175—177°. This is cyclised to *Et* 1:9-phenylenecarbazole-3:6-dicarboxylate, m.p. 185—187°, hydrolysed to the acid, m.p. >360°, which gives salts with alkaloids which dissociate on attempted crystallisation. *Et* 9-phenylcarbazole-3:6-dicarboxylate has m.p. 139—141°. Bromination of (I) gives successively 3(?) -bromo-, m.p. 205—210°, and 3:6(?) -dibromo-1:9-phenylenecarbazole, m.p. 202—209°. HNO_3 and I with (I) afford iodotritro-1:9-phenylenecarbazole, m.p. >340°. F. R. S.

m-Derivatives of acridine. X. Preparation of 2-chloro-7-methoxy-5-(8-diethylamino- α -methylbutyl)aminoacridine. N. S. DROZDOV (J. Gen. Chem. Russ., 1938, 8, 1192—1193).—5-Chloro-4'-methoxydiphenylamine-2-carboxyl chloride and $\text{NH}_2\text{-CHMe-}[\text{CH}_2]_3\text{-NEt}_2$ in C_6H_6 are heated for 30 min. at the b.p., POCl_3 is added, and boiling is continued for 7 hr., when 2-chloro-7-methoxy-5-(8-diethylamino- α -methylbutyl)aminoacridine is obtained in 81% yield. R. T.

meso-Derivatives of acridine. XIV. Alkylated 5-chloroacridines. N. S. DROZDOV (J. Gen. Chem. Russ., 1939, 9, 1456—1457).—10-Methylacridone and SO_2Cl_2 in $\text{C}_2\text{H}_4\text{Cl}_2$ yield a Cl-derivative, which with NH_2Ph affords 9-anilino-10-methylacridone, new m.p. 246—250°. 5-Chloro-3-methylacridine and $p\text{-C}_6\text{H}_4\text{Me-SO}_3\text{Me}$ (I) (1 hr. at 130°) give 3:10-dimethylacridone. (2:5-Dichloro-7-methoxyacridone and (I) (50 min. at 130°) yield unstable 2:5-dichloro-7-methoxy-10-methylacridine 10-*p*-toluenesulphonate, which readily decomposes into 2-chloro-7-methoxy-10-methylacridone and $p\text{-C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$. R. T.

Derivatives of acridine-5-aldehyde. (SIGNA.) L. MONTI (Gazzetta, 1939, 69, 749—752).—This aldehyde (I) with COPhMe in 15% NaOH or in EtOH (and *sec.* base) gives 5-(phenacylidenemethyl)acridine, m.p. 212—214°. In EtOH (NHMe_2), 5-(2'-hydroxy-4'-methoxy-, m.p. 196—198°, and 5-(2'-hydroxy-3':4'-dimethoxy-phenacylidenemethyl)acridine, m.p. 238—240°, are similarly prepared. In vaseline at 150° (bath), (I) (or its NaHSO_3 compound) and $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{-NH}_2$ give 5-(*p*-amidodisulphonylanilomethyl)acridine, m.p. 248—250°. E. W. W.

Reaction of sodium nitroprusside with hydantoin. G. TRAVAGLI (Annali Chim. Appl., 1939, 29, 479—481).—Hydantoin with Na nitroprusside in dil. aq. NaOH at 0° affords a complex,

$\text{Na}_3[(\text{CN})_5\text{Fe-NO-CH} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{NH} \end{smallmatrix}]$, hydrolysis of which gives parabanic acid and NH_4OH ; the mother-liquor on keeping yields $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$.

F. O. H.

Thiobarbituric acids.—See B., 1940, 87.

Reactions of pyrazolone derivatives. G. LOSCO (Gazzetta, 1939, 69, 639—646).—Methenylbis-4-(1-phenyl-3-methyl-5-pyrazolone) (I) with aq. NH_2OH in dioxan gives 1-phenyl-3-methyl-5-pyrazolone (II) and the *oxime* (III), m.p. 170—174° (decomp.), of its 4-aldehyde, from which (III) is also prepared. At 170—175°, (III) gives bis-(5-keto-1-phenyl-3-methyl-4-pyrazole), (I), and the 4-CN derivative (IV) (cf. A., 1938, II, 505) of (II). With MeI-MeOH at 130—135°, (IV) gives 4-cyano-1-phenyl-2:3-dimethyl-5-isopyrazolone, m.p. 224—225°, which in boiling conc. HCl yields 1-phenyl-2:3-dimethyl-5-isopyrazolone-4-carboxylamide, m.p. 241—243°, and, on prolonged boiling, antipyrine (V). With HCO-NHPh at 140—150° (but not with other anilides), (II) gives (I), and 3-methyl- and 1:3-diphenyl-5-pyrazolone react similarly. With HCO-NH_2 and HCO-NH-NHPh , (II) also gives (I). (V) does not react in this way.

E. W. W.

Pyrazolones [photographic colour developers].—See B., 1940, 89.

Transformation of isooxazole-3-carboxylic acids into pyrazole derivatives. [I.] II. S. CUSMANO (Gazzetta, 1939, 69, 594—601, 621—628).—I. 5-Phenylisooxazole-3-carboxylic acid heated with NHPh-NH_2 gives 5-amino-1:3-diphenylpyrazole (cf. Justoni *et al.*, A., 1938, II, 206), probably by way of $\text{CH}_2\text{Bz-CN}$ and its hydrazone.

II. 5-*p*-Nitrophenylisooxazole-3-carboxylic acid similarly gives 5-amino-1-phenyl-3-*p*-nitrophenylpyr-

azole (I), m.p. 185° (*Ac* derivative, m.p. 210°; *CHPh*: derivative, m.p. 175°), which with AcOH-NHO_2 gives a product separated by 5% KOH-EtOH into the 4-oximino-derivative (5-imino-4-oximino-1-phenyl-3-p-nitrophenylpyrazoline), decomp. $\sim 290^\circ$ (converted by conc. HCl into a substance, $\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_4$, m.p. 209°), of (I) in its imine form, and a substance, $\text{C}_{30}\text{H}_{21}\text{O}_2\text{N}_9$, m.p. 310°. E. W. W.

Action of methyl iodide on Schiff's bases of phenylmethylpyrazole-aldehyde and benzaldehyde. M. PASSERINI and G. LOSCO (*Gazzetta*, 1939, 69, 658—664).—Di-*p*-phenetylformamidine and 5-keto-1-phenyl-3-methylpyrazole heated in EtOH give 5-keto-1-phenyl-3-methyl-4-*p*-phenetyliminomethylpyrazole (I), m.p. 144—146°, which with MeI at 100—105° gives its 2-methiodide, m.p. 210—212° (decomp.), hydrolysed by 8% KOH to 5-keto-1-phenyl-2:3-dimethylpyrazole-4-aldehyde, m.p. 216—217° (*phenylhydrazone*, m.p. 190—192°; *oxime*, m.p. 220—221°; *semicarbazone*, decomp. 204—208°). At 120—130°, (I) and MeI give a product, m.p. 190°, hydrolysed by dil. NaOH to *p*-phenetyltrimethylammonium iodide (II), decomp. 230—235° (corresponding *nitrate*, m.p. 175—176°). *p*- $\text{OEt-C}_6\text{H}_4\text{-N:CHPh}$ and MeI at 120—130° give a product which in boiling H_2O gives (II). *p*- $\text{C}_6\text{H}_4\text{Me-N:CHPh}$ similarly yields *p*-tolyltrimethylammonium iodide (sublimes). E. W. W.

Reaction between allantoin and phenylhydrazine. E. CIMA (*Gazzetta*, 1939, 69, 664—667).—Allantoin and NHPh-NH_2 at 190—200° evolve NH_3 , giving a compound, $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}_7$, m.p. 163°, of diphenylcarbazine and phenylsemicarbazide, and 1:3-dianilino-5-ketotetrahydroglyoxaline [or possibly 4-anilino-5(or 6)-keto-1-phenylhexahydro-1:2:4-triazine], m.p. 173—175°, with, under certain conditions, an isomeride, m.p. 125°, of the last, into which this is converted when heated. E. W. W.

Pyrrole-indole group. Series II. XXVI. Dehydrogenation by means of sulphur: 3:3'-di-indolyl from indole. B. ODDO and (SIGNA.) L. RAFFA (*Gazzetta*, 1939, 69, 562—568).—Indole and S at 115—125° (sealed tube) give α -3:3'-di-indolyl (I) (cf. Gabriel *et al.*, A., 1923, i, 706) [*benzeneazoderivative*, m.p. 162—165° (softens 158°)]. At higher temp. S compounds are formed. With $\text{NaNO}_2\text{-AcOH}$, (I) gives a compound, $\text{C}_{16}\text{H}_{10}\text{O}_2$, m.p. 270° (decomp. from 245°). (I) forms with difficulty a *dipicrate*, m.p. 189° (explosive decomp.). E. W. W.

Reactions with amyl nitrite. IV. T. AJELLO (*Gazzetta*, 1939, 69, 646—658).—2-Methylindole and $\text{C}_6\text{H}_{11}\text{O}\cdot\text{NO}$ (I) give under certain conditions a small amount of a cryst. product, decomp. 222° (explosive). 2-Phenylindole with (I) in Et_2O gives the 3-oximino- (II) and in boiling C_6H_6 the 3- NO_2 -derivatives (III); with (I) in C_6H_6 , (II) gives (III). In Et_2O , (I) converts 1-hydroxy-2-phenylindole into 2-phenylisatogen (IV), and 3:3'-diketo-2:2'-diphenyl-1:1'-di-indolyl (V), m.p. 225°. [The same product was regarded by Angeli *et al.* (A., 1907, i, 153) as 3-hydroxy-2-phenylindole, but this was shown by Kalb *et al.* (A., 1912, i, 726) to have different properties.] Al-KOH , or better aq. NH_2OH in EtOH , reduces (V) to 3:3'-dihydroxy-2:2'-diphenyl-1:1'-di-indolyl (VI), m.p.

180—182° (cf. Kalb, *loc. cit.*) (*Bz* derivative, m.p. 238°). (I) converts (VI) into (V); with (I) in Et_2O , (V) slowly gives (IV). In AcOH , 30% H_2O_2 oxidises (VI) to 2-phenylindolone. E. W. W.

Condensation of isatin and urea. E. BUREŠ and J. HADÁČEK (*Časop. Českoslov. Lék.*, 1937, 17, 252—257).—Isatin and $\text{CO(NH}_2)_2$ condense to form a pink glass, m.p. 199—200°, with odour of bitter almonds. Hexagonal prisms are obtained by crystallisation, mol. wt. 239, mean N content 24.62%, forming metallic salts containing 26.12% Ag , 19.66% Hg , 4.68% Bi , 63.13% Pb . Bromination gives yellow-orange plates (Br 35.68%, N 7.16%), m.p. 245—246°. F. R.

Triazolium salts. IV. Reduction of benztriazolium salts. F. KRÖLLPFEIFFER, W. GRAULICH, and A. ROSENBERG (*Annalen*, 1939, 542, 1—13).—Reduction ($\text{Na}_2\text{S}_2\text{O}_4$, aq. NaOH ; method: A., 1935, 359) of 1:2-dimethyl-1:2:3-benztriazolium methosulphate (I) gives approx. equal amounts of *o*- $\text{NHMe-C}_6\text{H}_4\text{-N:NMe}$ (II) and a compound, $\text{C}_8\text{H}_{11}\text{N}_3$ (III), b.p. 110—111°/1 mm., which is not *o*- $\text{NHMe-C}_6\text{H}_4\text{-NH-N:CH}_2$ but may be *o*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-NMe-N:CH}_2$. Reduction of (I) with $\text{Na}_2\text{S}_2\text{O}_4$ in boiling 2*N*- NaOAc affords *o*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-NHMe}$ and NH_2Me . The violet hydrochloride from (II) and $\text{Et}_2\text{O-HCl}$ rearranges rapidly to a colourless salt, presumably *o*- $\text{CH}_2\text{-N-NH-C}_6\text{H}_4\text{-NHMe.HCl}$ (together with a little of a substance, $\text{C}_{18}\text{H}_{16}\text{N}_6$, decomp. 275°), attempted purification of which results in fission to NH_4Cl and 1-methylbenziminazole (IV). Boiling 2*N*- HCl similarly converts (II) into (IV). The *Ac* derivative, m.p. 193—194°, of (II) is reduced (Zn dust, EtOH-AcOH) to 1:2-dimethylbenziminazole; boiling 2*N*- HCl also gives (IV). Attempted thermal rearrangement of (II) was unsuccessful; boiling 2% EtOH-NaOEt affords a little of a compound, $\text{C}_8\text{H}_9\text{N}_3$, decomp. $\sim 120^\circ$ (according to rate of heating) [*picrate*, decomp. 135—136°; *Ac* derivative, m.p. 120—121° (accompanied by a substance, decomp. $\sim 310^\circ$)]. The hydrochloride from (III) with boiling EtOH also gives (IV) and NH_4Cl ; the *picrate* of (IV) is obtained directly from (III) and MeOH-picric acid . The *Ac}_2* (V), m.p. 135—136°, and *Ac}_1* derivative, m.p. 92—93° [from (V) and $\text{EtOH} + 2\text{N-NaOH}$], of (III) are both converted by boiling 2*N*- HCl into (IV), some 3-methyl-5:6-benz-1:2:4-triazine, m.p. 95—96° (cf. Bischler, A., 1890, 148), and resinous material. 1:3-Dimethyl-1:2:3-benztriazolium methosulphate, m.p. 97—98° [from 1-methylbenztriazole and Me_2SO_4 ; a little (I) is also formed], is reduced (Zn dust, 2*N*- HCl) to *o*- $\text{C}_6\text{H}_4(\text{NHMe})_2$ (VI); $\text{Na}_2\text{S}_2\text{O}_4\text{-aq. NaOAc}$ is without action but $\text{Na}_2\text{S}_2\text{O}_4\text{-aq. NaOH}$ gives α -*o*-methylaminophenyl- α -methylhydrazine (VII), b.p. 142—143°/14 mm., which with PhCHO-AcOH and Ac_2O affords 2-phenyl-1:3-dimethyl- and 2-hydroxy-1:2:3-trimethyl-2:3-dihydrobenziminazole, respectively. Short treatment of (VII) with boiling 2*N*- HCl gives 2:3-di(methylamino)-5:10-dimethylphenazonium dichloride ($+2\text{H}_2\text{O}$), m.p. 190—195° (according to rate of heating) [also obtained (method: Fischer, A., 1904, i, 349) by oxidation (FeCl_3) of (VI)]; the

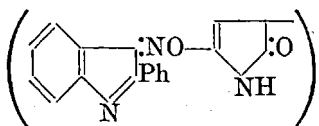
intermediate dihydrophenazine is oxidised by 1 mol. of (VII), whereby (VI) and NH_4Cl are produced.

H. B.

Constitution of yeast-rihonucleic acid. III. Nature of the phosphatase-resistant group. J. M. GULLAND and (Miss) E. M. JACKSON (J.C.S., 1939, 1842—1844; cf. A., 1938, III, 1051).—Dephosphorylation of yeast-rihonucleic acid with mixed bone-phosphomonoesterase and Russell's viper venom gives in the nucleotide fraction adenine and a nucleotide, $\text{C}_9\text{H}_{14}\text{O}_8\text{N}_3\text{P}$, possibly isomeric with cytidylic acid, together with guanine, guanosine, and uridine. Sweet-almond emulsin effects only 75% dephosphorylation and examination of the products suggests that the course of the reaction is the same.

F. R. S.

Constitution of nitrosopyrrole-black. II. G. ILLARI (Gazzetta, 1939, 69, 668—674; cf. A., 1939, II, 285).—The 2'-pyrrolinyl ether of 3-oximino-2-phenylpyrrole in boiling AcOH slowly gives a "black" (I), $\text{C}_{38}\text{H}_{24}\text{O}_5\text{N}_6$, no m.p., stable to 10% KOH in H_2O or EtOH, oxidised by $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ to $o\text{-CO}_2\text{H-C}_6\text{H}_4\text{-NHBz}$ (II) and $\text{H}_2\text{C}_2\text{O}_4$, by H_2O_2 in 5% KOH to a sol. K_2 salt of the compound, $\text{C}_{36}\text{H}_{24}\text{O}_7\text{N}_6$, and by KOH-KMnO_4 to (II). The annexed structure is proposed for (I).



E. W. W.

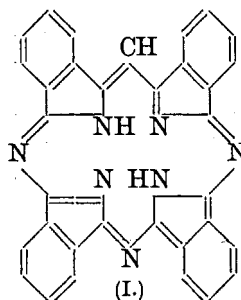
Chlorophyll. XCII. Synthesis of rhodoporphyrin- γ -carboxylic anhydride; synthetic rhodins and verdins. H. FISCHER and C. G. SCHRÖDER (Annalen, 1939, 541, 196—202).—Mesoverdin ester II (cf. A., 1939, II, 230) is oxidised ($\text{KMnO}_4\text{-COMe}_2$ at 0°) to the green rhodoporphyrin- γ -carboxylic anhydride, m.p. $250\text{--}251^\circ$ (previous sintering), identical with that [m.p. 260° (sinters at 250°)] obtained from phæoporphyrin- a_5 . Mesoporphyrin XIII (2:3:5:8-tetramethyl-1:4-diethylporphyrin-6:7-dipropionic acid) is converted (oleum) into mesorhodin XIII (Me ester, m.p. 275°) and thence by $\text{NH}_2\text{-CO-NH-NH}_2\text{-HCl}$ into mesoverdin XIII (Me ester, m.p. 241°). Similarly, mesoporphyrin II Me₂ ester (Me₂ 1:3:5:7-tetramethyl-4:8-diethylporphyrin-2:6-dipropionate) gives, as sole product, mesorhodin Me₁ ester II, m.p. 240° (previous sintering), and thence a verdin, $\text{C}_{35}\text{H}_{36}\text{O}_3\text{N}_4$, m.p. $222\text{--}223^\circ$ (previous sintering), not identical with mesoverdin ester I or II. Synthetic mesoporphyrin IX gives rise to the same verdins (*loc. cit.*) as are obtained from the natural product; the last is thus considered to be homogeneous. The rhodin from 1:3:5:7-tetramethyl-2:4-diethyl-6: γ -ethyleneporphyrin-8-propionic acid (the deoxophylloerythrin of A., 1935, 1134; prep. of which also gives an isomeric phylloerythrin) has m.p. 274° .

H. B.

Carboxyl and amino-groups of bilirubin. W. L. DULIÈRE (Bull. Soc. Chim. biol., 1939, 21, 1181—1184).—The salt obtained from bilirubin (I) and CaCl_2 in aq. medium contains 5.1% of Ca, but 9.05% in MeOH-EtOH medium. Treatment of (I) with HNO_3 indicates that the $\text{NH}_2\text{-N}$ content is 3.78% at first but, after ~12 hr., reaches 7%. These

results, which indicate that (I) is $\text{C}_{53}\text{H}_{54}\text{N}_2(\text{NH}_2)_6(\text{CO}_2\text{H})_6$, are explained by supposing that in aq. media part of the acidity due to CO_2H is neutralised by 1.5 N present as free NH_2 and that in alcohol this is blocked. W. McC.

Phthalocyanines and related compounds. XV. Tetrabenztriazaporphin: its preparation from phthalonitrile and a proof of its structure. P. A. BARRETT, R. P. LINSTAD, and G. A. P. TUEY. Preliminary X-ray investigation. J. M. ROBERTSON. XVI. Halogenation of phthalocyanines. P. A. BARRETT, E. F. BRADBROOK, C. E. DENT, and R. P. LINSTAD (J.C.S., 1939, 1809—1820, 1820—1828).—XV. Phthalonitrile and MgMeI condense in cold Et_2O , and when the solvent is removed and the residue heated with a little H_2O , Mg tetrabenztriazaporphin is obtained. After removal of Mg by acid



tetrabenztriazaporphin (I), $\text{C}_{33}\text{H}_{19}\text{N}_7$, is isolated in plates or needles. The homogeneity of the substance has been established by absorption spectra measurements and the formula (I) indicates a resonance hybrid. (I) forms Cu, Zn, Mg, and Fe^{II} derivatives of the type $\text{C}_{33}\text{H}_{17}\text{N}_7\text{Metal}^{II}$; Cu-mono-chlorotetrabenztriazaporphin is also obtained from (I) and CuCl_2 .

Oxidation of (I) with $\text{Ce}_2(\text{SO}_4)_3$ proceeds quantitatively according to $\text{C}_{33}\text{H}_{19}\text{N}_7 + 5\text{O} + 5\text{H}_2\text{O} = 4\text{C}_8\text{H}_5\text{O}_2\text{N} + \text{CO}_2 + 3\text{NH}_3$. X-Ray investigation of (I) indicates that a centre of symmetry is present, which is probably due to the fact that the mols. display a statistical centre of symmetry in the crystal. Phthalonitrile and LiMe in varying proportions give mixtures containing some (I) and the diaza-compound and phthalocyanine (II); with LiBu^a , a mixture of (I) and (II) is obtained. With excess of LiMe in cyclohexanol at 200° , 3-amino-1:1-dimethylisoindeole, m.p. 144° (picrate, m.p. 255°), is isolated. The mechanism of the formation of (I) is discussed.

XVI. Under mild conditions, (II) reacts with free halogens to yield additive compounds (octabromide; chlorides), which can be hydrolysed to (II). At high temp. and in the presence of catalysts, the benzene rings are substituted (bromo-, 3- and 4-tetrachloro-, 3:6- and 4:5-octachloro-, and dodecachlorophthalocyanines). The orientation of the products has been determined by degradation and measurement of absorption spectra. Other halogenating agents, e.g., SO_2Cl_2 , SOCl_2 , behave similarly, giving substitution products only. The most highly halogenated substances contain 12 to 13 atoms of halogen and are bright green. Metallic derivatives can also be obtained; the properties are recorded.

F. R. S.

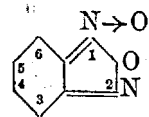
isoOxazolecarboxylamides.—See B., 1940, 87.

isoBenzoxazoles. III. W. BORSCHKE and W. SCRIBA (Annalen, 1939, 541, 283—292; cf. A., 1939, II, 454).—2-Alkylisobenzoxazoles are obtained from $o\text{-C}_6\text{H}_4\text{Br-Calk-N-OH}$ and aq. MeOH-KOH at $110\text{--}150^\circ$ (cf. Meisenheimer *et al.*, A., 1926, 405). The oxime, m.p. 129° , of $o\text{-C}_6\text{H}_4\text{Br-COMe}$ [prep. from

o-C₆H₄Br·CN (I) and MgMeI (3 mols.)] thus gives 2-methylisobenzoxazole; the *oxime*, b.p. 164—172°/16 mm., of *o*-C₆H₄Br·COEt [from (I) and MgEtBr; 2:4-dinitrophenylhydrazones, m.p. 115—116°] affords impure 2-ethylisobenzoxazole; the *oxime*, m.p. 116°, of *o*-C₆H₄Br·CO·CH₂Ph, b.p. 206—208°/15 mm. [from (I) and CH₂Ph·MgCl; 2:4-dinitrophenylhydrazones, m.p. 149°], yields 2-benzylisobenzoxazole, m.p. 87°; the *oxime* (II), m.p. 131—132° (cf. Claus, A., 1892, 1200), of 2-bromo-5-methylacetophenone (III), b.p. 132—136°/15 mm. (2:4-dinitrophenylhydrazones, m.p. 170°), gives 2:4-dimethylisobenzoxazole. The results with (II) differ from those of Claus (*loc. cit.*), whose *oxime* may be a stereoisomeride of (II) or 2:5:1-C₆H₃MeBr·CMe·N·OH. Gradual addition of Sn powder to a well-shaken, cooled mixture of 1:4:3-C₆H₃MeBr·NO₂, oleum, and graphite powder affords 1:4:3-C₆H₃MeBr·NH₂, converted into 4-bromo-*mtolunitrile*, m.p. 65°, which with MgMeI gives (III). MgPr²Br and MgBu²Br do not react with (I). *o*-C₆H₄Br·CO₂Me and MgMeI (1.2 mols.) yield *o*-bromophenyl-dimethylcarbinol, b.p. 128—130°/16 mm. *o*-C₆H₄Cl·CN and MgMeI afford *o*-C₆H₄Cl·COMe [2:4-dinitrophenylhydrazones, m.p. 206°; semicarbazones, m.p. 178—179° (lit. 159—160°)]. *o*-C₆H₄Br styryl ketone, b.p. 234—238°/14 mm. (2:4-dinitrophenylhydrazones, m.p. 236—237°), does not react with NH₂OH. 5-Nitro-1-phenyl-3-methylisindazole, m.p. 131—132° (from 5:2:1-NO₂·C₆H₃Br·COMe and NHPH·NH₂·HCl in MeOH at 150°), is reduced (H₂, Pd-C, MeOH) to the 5-NH₂-compound, m.p. 127—128° (Bz derivative, m.p. 160—161°) (together with some ? azoxy-compound, m.p. 336°), which is deaminated (*iso*-C₆H₁₁·O·NO in MeOH-HCl followed by H₃PO₂) to 1-phenyl-3-methylisindazole, m.p. 73—74°.

H. B.

Structure of *o*-dinitrosobenzenes. G. TAPPI and (SIGNA.) A. DEMORRA (Gazzetta, 1939, 69, 708—713).—The benzfurazan oxide formula (A) for “dinitrosobenzene” (cf. Green *et al.*, J.C.S., 1912, 101, 2452) is confirmed. Benzfurazan and its 3- and 4-Me derivatives produce abnormally low depression of the m.p. of benzfurazan 1-oxide (I) and of its 6- (II) and 4-Me derivative (III), as do (II) and (III) of the m.p. of (I), thus showing formation of solid solutions and hence furazan structure in (I), (II), and (III). E. W. W.



(A.)

Derivatives of 3:3'-dipyridyl and of 3:3'-dipyridylene oxide. G. JACINI and (SIGNA.) A. SALINI (Gazzetta, 1939, 69, 717—721).—4:5-Dihydroxy-2:7- [not 2:6- (cf. A., 1939, II, 286)]-dimethyl-1:8-phenanthroline with KMnO₄ in 2% KOH gives 4:4'-dihydroxy-6:6'-dimethyl-3:3'-dipyridyl-2:2'-dicarboxylic acid (I), m.p. <350°. In conc. H₂SO₄ this gives the *anhydride*, m.p. 330° (decomp.), from which the *monoamide*, m.p. 290° (decomp.), and *monophenylhydrazide*, m.p. 310° (decomp.), of (I) are prepared. When heated with powdered glass, (I) gives 6:6'-dimethyl-3:3'-dipyridyl-4:4'-ene oxide [2:2'-dimethyl-3:6-diazadibenzfuran], m.p. 156°.

E. W. W.

Dioximes. CXXIV. G. TAPPI and U. DI VAJO (Gazzetta, 1939, 69, 615—620).—The dipole moments

of derivatives of glyoxime peroxide (I) in C₆H₆ are determined, and compared with those of 1:2:5-oxadiazoles, and with vals. calc. for oxides of the latter and the (lower) vals. calc. for 1:2:3:6-dioxadiazines. It is concluded that the Me₂, Me Et, and probably the Ph₂ derivatives of (I) are dioxadiazines, as are the Me Ph and Me *p*-OMe·C₆H₄ derivatives, m.p. 62° and 79°, respectively. The Me Ph and Me *p*-OMe·C₆H₄ derivatives, m.p. 96° and 99°, respectively, are considered to be oxadiazole oxides, in agreement with previous views. E. W. W.

Thiazolidines.—See B., 1940, 88.

Preparation of 6-chlorophenylenthiazthionium compounds, and their stability. M. K. BEZZUBETZ and V. A. IGNATIUK-MAISTRENKO (J. Appl. Chem. Russ., 1939, 12, 1137—1142).—*p*-C₆H₄Cl·NH₂ and S₂Cl₂ in AcOH, heated at 20—65° for 12 hr., give 6-chlorophenylenthiazthionium chloride (I) in 60% yield; in other solvents (C₆H₆, CCl₄, ligroin) the yields are much smaller. Both (I) and its corresponding base are very unstable, rapidly decomp. in presence of light and air. The base is obtained pure by extracting the crude product with Et₂O, followed by recrystallisation from CCl₄.

R. T.

Cyanine dyes.—See B., 1940, 89.

Chemical study of *Ammothamnus Lehmannii*. Bge. I. G. V. LAZUREVSKI and A. S. SADIKOV (Bull. Univ. Asie Centr., 1937, No. 22, 171—176).—Two alkaloids, sophocarpine and *ammothamnine*, C₁₆H₂₇O₃N₂, m.p. 204—205° (*picrate*, m.p. 207—208°; *hydriodide*, m.p. 188—189°), have been isolated from the plant. In addition, the roots contain 8%, and the rest of the plant 3%, of a red substantive dye for silk, wool, and leather.

R. T.

Synthesis of isomerides of hydroquinine. I. (5-Ethyl-2-quinuclidyl)-(6-methoxy-8-quinolyl)-carbinol. M. V. RUBTZOVA (J. Gen. Chem. Russ., 1939, 9, 1493—1506).—8-Cyano-6-methoxyquinoline is hydrolysed (65% H₂SO₄, at the b.p.) to 6-methoxyquinoline-8-carboxylic acid, m.p. 196—197° [*sulphate*, +3H₂O, m.p. 243—245° (decomp.)], the Et ester, m.p. 64.5—65.5°, of which is added to the Et ester of benzoylhomocincholipon in an Et₂O-EtOH solution of NaOEt. The solvent is distilled off, and the residue, heated for 4 hr. at 80°, yields 6-methoxy-8-quinolyl β-(1-benzoyl-3-ethyl-4-piperidyl)-α-carboethoxyethyl ketone, m.p. 54—56°, which is hydrolysed (50% H₃PO₄; 4 hr. at the b.p.) to 6-methoxy-8-quinolyl β-(3-ethyl-4-piperidylethyl ketone (isohydroquinotoxine) (I), an oil [*platinichloride*, chars at 220—240°, decomp. 282—285°; *dihydrobromide*, m.p. 193—194° (decomp.)]; *picrate*, an oil; *dipicrate*, m.p. ~100°]. (I) is brominated (Br in HBr, at 80°), and the product is shaken with aq. Na₂CO₃ and C₆H₆, when 6-methoxy-8-quinolyl 5-ethyl-2-quinuclidyl ketone (isohydroquinone) (II), m.p. 153—154°, [*α*]_D²⁵ +51.7° in CHCl₃, [*dipicrate*, m.p. 172—173°; *dipicrolonate*, m.p. 203—205° (decomp.)], is isolated from the C₆H₆ layer. (II) is hydrogenated (Pd-black) to (probably) α-(6-methoxy-8-quinolyl)-γ-(3'-methylpiperidyl)propanol (isohydrotoxinol), an oil [*hydrochloride* of 1'-NO-derivative, m.p. 140° (decomp.)]. With Al(OPrⁿ)₃ in

$\text{Pr}^{\text{B}}\text{OH}$ (18 hr. at 90–95°) (II) gives (6-methoxy-8-quinolyl)-(5-ethyl-2-quinuclidyl)carbinol (isohydroquinine) (III) in three diastereoisomeric forms: (i), m.p. 177.5–178°; $[\alpha]_{\text{D}}^{20} + 135.9^\circ$ in EtOH, (ii), a glass, $[\alpha]_{\text{D}}^{20} + 52.0^\circ$ in EtOH (picrolonate, m.p. 199–200°), and (iii), a glass, $[\alpha]_{\text{D}}^{20} + 65.4^\circ$ in EtOH (picrolonate, m.p. 154–155°). The isomerides of (III) have no antimalarial action, but retain the anaesthetic action of hydroquinine. (II) is highly toxic. R. T.

Strychnine compound of Bordeaux B (strychnine-azorubrate). D. B. DOTT (Pharm. J., 1939, 143, 527; cf. A., 1939, II, 41).—A modified method for extracting the strychnine is described.

A. T. P.

Strychnine and brucine. Alkaline degradation. I. Strychnine. II. Brucine. R. H. SIDDIQUI (J. Indian Chem. Soc., 1939, 16, 396–398; 399–401).—I. Strychnine (structure discussed) and $\text{KOH-H}_2\text{O}$ (3 : 1) distilled from a Cu flask give a compound, $\text{C}_8\text{H}_{11}\text{N}$ (I) [picrate, m.p. 141–142°, is identical with that, m.p. 143–144°, of Clemo (A., 1937, II, 38)], and a little of a substance (picrate, m.p. 195–196°). (I) is not 2-methyl-4-ethylpyridine.

II. Brucine and KOH similarly give (I), and compounds (?) $\text{C}_8\text{H}_9\text{N}$ (picrate, m.p. 143–144°), and (?) $\text{C}_{11}\text{H}_{11}\text{N}$ or $\text{C}_{11}\text{H}_{13}\text{N}$ [picrate, m.p. 172° (softens at 163–168°)]. A. T. P.

Argentine plants. I. Hypaphorine from *Erythrina cristagalli*. V. DEULOFEU, E. HUG, and P. MAZZOCCO (J.C.S., 1939, 1841–1842).—Hypaphorine (tryptophan betaine) [flavianate, m.p. 235° (decomp.)] has been isolated from the seeds.

F. R. S.

Tetrandrine picrate.—See A., 1940, III, 84.

Alkaloids from *Rauwolfia serpentina*. S. SIDDIQUI (J. Indian Chem. Soc., 1939, 16, 421–422).—Roots and root-bark of *R. serpentina* from the Dun valley give alkaloids allied to the ajmaline series (cf. A., 1935, 636). isoAjmaline (I), m.p. 264–266°, an isomeride, neoajmaline, m.p. 205–207° [convertible into (I) at 270° or by KOH-EtOH], alkaloids, m.p. 220° and 234°, and traces of ajmalinine and serpentinine are isolated. The yellow oxidation bases of the plant from the Bihar district (*loc. cit.*) are not formed in the milder conditions of the Dun valley.

A. T. P.

Nitration of diphenyliodonium nitrate. R. B. SANDIN, F. T. McCURE, and F. IRWIN (J. Amer. Chem. Soc., 1939, 61, 3061–3063).— $\text{Ph}_2\text{I-NO}_3$ is treated with $\text{HNO}_3\text{-H}_2\text{SO}_4$ at 0°–room temp. and then converted by KI into $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{I-I}$, which is decomposed by heat into $\text{C}_6\text{H}_4\text{I-NO}_2$. <18.5% of *p*-nitration (cf. Challenger *et al.*, A., 1934, 1118) is indicated by thermal analysis of the product. 10% of *p*- $\text{C}_6\text{H}_4\text{I-NO}_2$ is isolated. Pyrolysis of $(m\text{-NO}_2\cdot\text{C}_6\text{H}_4)_2\text{I-I}$ gives no *p*- $\text{C}_6\text{H}_4\text{I-NO}_2$. R. S. C.

Dissociation in alcohols of compounds of the type R-HgPh , where R is an acid residue. M. M. KOTON (J. Gen. Chem. Russ., 1939, 9, 1622–1625).—The compounds $\text{R-CO}_2\text{HgPh}$ decompose when heated with alcohols at 125–175°, as follows: $\text{R-CO}_2\text{HgPh}$

$\rightarrow \text{HgPh}^+ + \text{R-CO}_2^-$; $2\text{R-CO}_2 + \text{EtOH} \rightarrow 2\text{R-CO}_2\text{H} + \text{MeCHO}$; $2\text{HgPh}^+ + \text{EtOH} \rightarrow 2\text{Hg} + 2\text{C}_6\text{H}_6 + \text{MeCHO}$; $\text{R-CO}_2\text{H} + \text{EtOH} \rightarrow \text{R-CO}_2\text{Et} + \text{H}_2\text{O}$. The velocity of the reactions in different solvents falls in the order $\text{iso-C}_5\text{H}_{11}\cdot\text{OH} > \text{EtOH} > \text{MeOH}$, and for different R in the order $\text{R} = \text{H} > o\text{-OH-C}_6\text{H}_4 > \text{OH-CHMe-CH}_2 > \text{OH-CHMe} > \text{Me} > \text{Et} > \text{Pr} > \text{C}_5\text{H}_{11} > \text{C}_{17}\text{H}_{35} > \text{Ph}$. R. T.

Mercury derivatives of aromatic acids and heterocyclic compounds.—See B., 1940, 88.

Synthesis of condensed selenophens by the action of acetylene on selenium. S. UMEZAWA (Bull. Chem. Soc. Japan, 1939, 14, 363–373; cf. A., 1936, 871).—If the fractions of higher b.p. obtained from the product of the action of purified C_2H_2 on Se are preserved isoselenophthen (I),

$\text{CH} \begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{CH} \\ \text{Se}\cdot\text{C}\cdot\text{CH} \end{array} \text{Se}$, m.p. 123–124.5° (picrate, m.p. 163–165°), slowly separates. (I) is converted by Br in well-cooled CS_2 into an intermediate, yellow additive product and ultimately into isotetrabromoselenophthen, $\text{C}_6\text{Br}_4\text{Se}_2$, m.p. 247.5° (corr.). Conc. or fuming HNO_3 oxidises (I) violently but the requisite amount of fuming HNO_3 transforms (I) in well-cooled Ac_2O into nitroisoselenophthen, m.p. 108–109.5°, which can be preserved in a coloured desiccator. Conc. H_2SO_4 decomposes (I) but converts it in presence of Ac_2O into isoselenophthendisulphonic acid [$\text{Ba} (+3\text{H}_2\text{O})$ and $\text{K} (+1.5\text{H}_2\text{O})$ salts; disulphonyl chloride, decomp. 234–236°]. The residues obtained from the isolation of (I) give fractions, b.p. 93–100°/14 mm. and 100–113°/14 mm., which, after removal of selenonaphthen and C_{10}H_8 , as picrates, afford “cis”-selenophthen (II),

$\text{CH} \begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{CH} \\ \text{Se}\cdot\text{C}\cdot\text{Se} \end{array} \text{CH}$, b.p. 90–93°/14 mm. This gives an amorphous product with aq. $\text{Hg}(\text{OAc})_2$ and appears to be transformed by HgCl_2 in aq. EtOH into “cis”-selenophthen mercurichloride. (II) is converted by an excess of Br in CS_2 at 0° into tetrabromo “cis”-selenonaphthen, m.p. 271–272° (decomp.). “trans”-

Selenophthen, $\text{CH} \begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{Se} \\ \text{Se}\cdot\text{C}\cdot\text{CH} \end{array} \text{CH}$, m.p. 51–51.5°, gives a picrate, m.p. 154–155.5°, and a Br_4 -derivative, m.p. 252.5–253° (decomp.). Selenonaphthen (III), $\text{CH}:\text{CH}\cdot\text{C}\cdot\text{CH} \begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{CH} \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{Se} \end{array} \text{CH}$, m.p. 50–51° (corr.), is isolated from the products of the action of C_2H_2 on Se by means of its picrate, m.p. 156–157° (corr.). *o*-Aminocinnamic acid is converted by diazotisation and treatment with KCNSe into *o*-selenocyanocinnamic acid, m.p. 171–173° (decomp.); this is transformed by KOH into *o*-selenolcinnamic acid, oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ to (III). H. W.

Colloid-chemical properties of thermolysed gelatin.—See A., 1940, I, 71.

Biological aspects of protein chemistry. M. BERGMANN (J. Mount Sinai Hospital, 1939, 6, 171; Comm. Sci. Pract. Brewing, 1939, No. 7, 21–32).—A lecture, the subjects critically discussed including: the composition and magnitude of the protein mol., with special reference to structural regularity; the peptide linkage and the attack thereon by protein-

ases; enzymic synthesis of peptide linkages, including specificity and thermodynamic considerations.

I. A. P.

Hydrolysis of gelatin by enzymes and by heating under pressure.—See A., 1940, III, 163.

Reaction between cephalin and hæmoglobins.—See A., 1940, III, 43.

Compounds between phosphatides and basic proteins.—See A., 1940, III, 43.

Identification of the halogen in organic [and inorganic] halogen compounds. D. W. WILSON and C. L. WILSON (J.C.S., 1939, 1956—1958).—A drop of inorg. halide solution or of solution from an org. Na micro-fusion is acidified with HNO_3 , treated with AgNO_3 , and evaporated. AgCl is roughly separated by dissolution in very dil. aq. NH_3 and AgBr by dissolution in aq. NH_3 (d 0.880), and each is crystallised from aq. NH_3 (d 0.880). Residual AgI is crystallised as (?) pyridinium salt from $\text{C}_5\text{H}_5\text{N}$. The crystals are identified microscopically. Limits are: one halogen alone 1, Cl' 1 in presence of Br' 10, Br' 1 in presence of Cl' 30, I' 1 in presence of Cl' or Br' 50 μg .

R. S. C.

Semimicro-Kjeldahl distillation apparatus.—See A., 1940, I, 84.

Submicro-determination of total and amino-nitrogen, amides, peptides, and adenylic acid.—See A., 1940, III, 176.

Determination of organic sulphur in gases. S. DOLDI (Annali Chim. Appl., 1939, 29, 542—550).—The method is based on hydrogenation (Pt at 800—850°) of org. S to H_2S , absorption in 10% CdCl_2 in dil. HCl , and iodometric titration.

F. O. H.

Semi-micro-analytical determination of methoxyl groups in organic compounds. E. B. LISLE (Analyst, 1939, 64, 876—877).— OMe is liberated as MeI by HI at 130°. The vapour is passed over a test paper steeped in a solution of PdCl_2 and $\text{C}_5\text{H}_5\text{N}$. The intensity of the brown colour developed on the test paper is compared with standard papers previously prepared.

E. C. B. S.

Pyridine phthalisation. S. SABETAY (Ann. Chim. Analyt., 1939, [iii], 21, 289—290).—Accurate results are obtained by the method described previously (A., 1938, II, 77) only when the procedure laid down is strictly followed. Data recorded for $\text{CH}_2\text{Ph}\cdot\text{OH}$ show that the hydrolysis of the $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ is completed by warming for 1 min., that the vol. of H_2O added is crit., and that prolonged heating (>1 min.) must be avoided. Details of procedure for the analysis of alcohols are given.

L. S. T.

Determination of paraldehyde. D. J. T. BAGNALL, A. SMITH and A. R. TANKARD (Analyst, 1939, 64, 857—861).—Paracetaldehyde is determined by conversion into MeCHO , which on distillation into $\text{NH}_2\text{OH}\cdot\text{HCl}$ forms the oxime and liberates HCl ,

which is titrated with NaOH . A procedure in cases of poisoning is recommended.

E. C. B. S.

[Determination of] sulphanilamide. E. M. HOSHALL (J. Assoc. Off. Agric. Chem., 1939, 22, 748—757).—Several published methods for the determination of sulphanilamide were critically examined and new methods evolved. Direct bromination was unsatisfactory. Indirect bromination ($\text{KBr}\text{--}\text{KBrO}_3$) (studied collaboratively) gives slightly high results, apparently owing to the formation of a sulphondibromoamide (I) from which Br is not completely liberated on acidification (HCl). Prep. (by HOBr) and analyses of (I) and its Ac derivative give low vals. Determination of the SO_2NH_2 group by hydrolysis [75% (vol.) H_2SO_4] and distillation of the free NH_3 from alkaline solution was collaboratively studied and found to give more accurate results. It is recommended that the latter be adopted as a tentative method and that indirect bromination be adopted as an alternative tentative method.

E. C. B. S.

Determination of salicylic acid by ferric chloride. G. ILLARI (Annali Chim. Appl., 1939, 29, 490—500).—The extents to which H_3BO_3 , H_3PO_4 , AcOH , $\text{H}_2\text{C}_2\text{O}_4$, tartaric, and citric acid, and various Na and K phosphates, oxalates, tartrates, and citrates interfere with the photometric determination of salicylic acid by FeCl_3 (0.5% in 0.01N- HCl) were determined. The results are discussed with respect to the probable reactions of FeCl_3 with the above substances.

F. O. H.

Rapid determination of nicotine. A. VERDA and E. HERZFELD (Z. anal. Chem., 1939, 118, 9—13).—The sample (5—20 g.) is mixed with 2 g. of MgO , 30 g. of NaCl , and 100 c.c. of H_2O and steam-distilled (300 c.c.) on to 3 g. of gum arabic. After filtration, a dilution series is prepared, each dilution being treated with a silicotungstic acid reagent, which gives an opalescence with nicotine (I). The opalescences are compared (cf. A., 1939, III, 98) with a standard series, the limiting val. of which corresponds with 0.31 mg. of (I).

L. S. T.

Herapathite reaction on aristoin. M. WAGENAAR (Pharm. Weekblad, 1939, 76, 1544—1545).—The appearance of the micro-cryst. ppt. when $\text{KI}\text{--}\text{I}$ is added to an acid solution of aristoin (quinine carbonate) is considerably delayed by the presence of some impurity. The addition of COMe_2 facilitates the reaction.

S. C.

Analysis of protein by means of deuterium-containing amino-acids. H. H. USSING (Nature, 1939, 144, 977).— NH_2 -acid containing D in the $\text{C}\text{--}\text{H}$ position is mixed with the hydrolysed protein, and then NH_2 -acid is isolated from the mixture by the usual methods. From the D content of the NH_2 -acid isolated the proportion in which the "heavy" NH_2 -acid added is diluted by the NH_2 -acid originating from the protein is calc.

L. S. T.

Polarographic micro-determination of cystine in protein hydrolysates.—See A., 1940, III, 176.

A., II.—Organic Chemistry

MARCH, 1940.

Formation of methane from carbon monoxide-hydrogen mixtures in contact with low-temperature coke.—See B., 1940, 113.

Induced pyrolysis of methane.—See B., 1940, 113.

Reaction of hydrogen and deuterium atoms with propane.—See A., 1940, 1, 120.

Catalytic cracking of aliphatic hydrocarbons. G. EGLOV, J. C. MORRELL, C. L. THOMAS, and H. S. BLOCH (J. Amer. Chem. Soc., 1939, 61, 3571—3580).—Mixed n - C_4H_8 are isomerised in presence of activated Al_2O_3 - SiO_2 at 385—600°, with some polymerisation and cracking; at 450—600° an apparent equilibrium mixture containing $24.1 \pm 1.5\%$ of $CH_2:CHMe$ is formed. n - C_5H_{10} at 400° (this and other reactions with the above catalyst) undergoes similar reactions, which give 50% of isopentenenes. n -Octenes at 375—400° suffer isomerisation, followed by cracking, the products containing much n - and *iso*- C_4H_8 . Cetene at 300—450° behaves similarly, but the branched-chain olefines are more readily cracked. Catalytic cracking of n - C_8H_{16} is 7—8 times as fast as is thermal cracking, gives more C_5 — C_7 products, and is effective at 525—570°. Cetane is catalytically cracked at 500°, giving 1 mol. of C_3 — C_5 products per mol. of cetane; n - and *iso*-products are formed. R. S. C.

Stability of polymorphous forms of normal hydrocarbons with long stretched chains and their derivatives. T. SCHOON (Ber., 1939, 72, [B], 1821—1827; cf. A., 1938, I, 348).—Röntgenographic investigation of the transition mechanism shows that the rhombic form of $C_{30}H_{62}$ is the practically stable modification. The monoclinic, high-temp. form (ϵ_2 -form) of stearic acid is probably completely stable since in this variety the units contain an abs. min. of free energy. H. W.

Peroxide effect in the addition of reagents to unsaturated compounds. XXIV. Addition of hydrogen iodide to propylene, α -bromopropylene, allyl chloride, and allyl bromide. M. S. KHARASCH, J. A. NORTON, and F. R. MAYO (J. Amer. Chem. Soc., 1940, 62, 81—86; cf. A., 1940, II, 9).—Contrary to Ingold *et al.* (A., 1931, 1391), $CH_2:CHMe$ and HI give only Pr^iI , whether or not air, H_2O , peroxides, antioxidants, or solvents are present. I, peroxides (which liberate I), or HgI_2 accelerate the reaction, probably by addition to give $CHMeI$ - CH_2I and reduction thereof by HI. In some solvents, a little high-boiling material (? $C_6H_{13}I$) is formed. Suppression by HI of the peroxide-catalysed "abnormal" addition of HBr is due to destruction of the peroxide. $CH_2:CH$ - CH_2Br and HI under all conditions give $CHMeI$ - CH_2Br ; the reaction is auto-

catalytic, as some I is liberated and up to 30% of Pr^iI halides are formed; I (or peroxides) catalyses the addition, probably owing to formation and reduction of CH_2I - CHI - CH_2Br ; in the simple reaction, the I is probably first obtained by formation of $CH_2:CH$ - CH_2I . In accordance with these views, $CH_2:CH$ - CH_2Cl , which has much less tendency to form the iodide, gives 90—100% of $CHMeI$ - CH_2Cl , b.p. 66.2°/50 mm., I and H_2O being catalysts. Various proportions of HI and $CHMe:CHBr$ with or without peroxides give $CHEtBrI$, b.p. 61.3°/20 mm., and $CHMeI$ - CH_2Br .

R. S. C.

Organo-alkali compounds. XV. Controlled 1:2 and 1:4 polymerisation of butadiene. K. ZIEGLER, H. GRIMM, and R. WILLER (Annalen, 1939, 542, 90—122).—An extension of previous work (Part XI; A., 1934, 864). Butadiene (I) (1.5—2.5 mols.) and LiBu (1 mol.) in Et_2O at 25—30° give (after decomp. with H_2O) octenes, dodecadienes (A), b.p. 74—90°/9 mm. [max. yield (34.4%) with 1.75 mols. of (I)], and products of higher b.p. Fractionation of (A) affords 75—80% of ϵ -vinyl- Δ^8 -decene, b.p. 79—81°/11 mm. [oxidised (CrO_3 - $AcOH$) to α - n -amylsuccinic acid], and 20—25% of Δ^8 -dodecadiene, b.p. 90—92°/12 mm., which are reduced (H_2 , Pd- $BaSO_4$, $EtOAc$) to ϵ -ethyl- n -decane (II), b.p. 94.7°/20 mm., and n - $C_{12}H_{26}$ (III), b.p. 104.6°/20 mm., m.p. -10.1°, respectively, thus proving the occurrence of 1:2 and 1:4 addition in the initial reaction. Quant. separation of (II) and (III) is best effected with a modified Podbielniak column (described). With (I) (1.5 mols.) and LiBu (1 mol.) in C_6H_6 at 100—115°, reaction occurs mainly by 1:4 addition; subsequent reduction of the octene-freed product affords a mixture of n -paraffins [(III), $C_{16}H_{34}$, $C_{20}H_{42}$, $C_{24}H_{50}$, and $C_{28}H_{58}$ are isolated]. At -50° in Et_2O 1:2 addition is the predominant reaction; (II), $\epsilon\eta$ -diethyldodecane, b.p. 135—136°/17 mm., and $\epsilon\eta$ -triethyltetradecane, b.p. 167—171°/17 mm., are similarly isolable. Analogous 1:2 and 1:4 addition also occurs with (I) and $CKPhMe_2$ (IV) at low and high temp., respectively; reduction of the appropriate fraction thus affords β -phenyl- β -methyl- δ -ethyloctane, b.p. 149°/20 mm. [synthesised from $CHEtBu$ - CH_2I and (IV) in Et_2O], and β -phenyl- β -methyldecane, b.p. 160°/20 mm. [also from n - $C_8H_{17}Br$ and (IV)], respectively. The mode of addition is not influenced to any appreciable extent by other reaction conditions [*e.g.*, solvent; rate of addition of (I)]; temp. is the decisive factor. In confirmation of the above results oxidation (O_3 followed by CrO_3 in $AcOH$) of the product from LiBu (1 mol.) and (I) (7 mols.) in methylcyclohexane at 150° gives ~60% of the calc. amount of pure $(CH_2:CO_2H)_2$, none of which is similarly obtained

from the product from (I) and (IV) at -80° . Passage of a mixture of EtCO_2H (2 mols.) and $n\text{-C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$ (1 mol.) over ThO_2 -pumice at 400° affords COEt_2 , $\text{CO}(\text{C}_5\text{H}_{11})_2$, and $\text{COEt}\cdot\text{C}_5\text{H}_{11}$ - n (V) (major product). The carbinol, b.p. $112^{\circ}/13\text{ mm.}$, from (V) and MgBuCl is dehydrated (conc. H_3PO_4 at $90\text{--}100^{\circ}/\text{vac.}$) and then reduced (H_2 , Raney Ni, 160°) to (II). H. B.

Condensations by sodium. XV. Reactions of disodium compounds with ethylidene and methylene chlorides. A. A. MORTON and J. T. MASSENGALE. **XVI.** Formation of decane in the Wurtz reaction. A. A. MORTON and G. M. RICHARDSON. **XVIII.** Possible conversion of sodium amyl into disodium amylidene. A. A. MORTON and G. M. RICHARDSON (J. Amer. Chem. Soc., 1940, 62, 120—123, 123—126, 129—131; cf. A., 1938, II, 409).—**XV.** $\text{CHBu}^{\text{a}}\text{Na}_2$ and CHMeCl_2 in light petroleum (b.p. $<45^{\circ}$) give 13% of $\text{CHMe}\cdot\text{CHBu}^{\text{a}}$, in agreement with the amount (17%) of $\text{CHBu}^{\text{a}}\text{Na}_2$ predicted by formation of $\text{CHBu}^{\text{a}}(\text{CO}_2\text{H})_2$ by CO_2 . Some CHPhNa_2 is also formed when Na, PhMe, and PhCl react in light petroleum; Me_2SO_4 and MeI show presence of 46 and 43% (yields of PhEt) of CH_2PhNa ; CO_2 indicates $\sim 15\%$ of other Na derivatives; CH_2Cl_2 and CHMeCl_2 give $\text{CH}_2\cdot\text{CHPh}$ and $\text{CHPh}\cdot\text{CHMe}$, respectively, although yields are $<4\%$. The styrenes are not formed by way of $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Cl}$, which is ineffective in this reaction. CH_2PhNa , produced by PhCl, is less reactive than when produced by $\text{C}_5\text{H}_{11}\text{Cl}$, probably because of the higher temp. (85°) needed. CH_2PhCl or CHPhCl_2 does not produce Na derivatives. $\text{Br}\cdot[\text{CH}_2]_5\cdot\text{Br}$ and CHPhCl_2 afford no evidence of Na_2 compounds.

XVI. The products formed from $\text{C}_5\text{H}_{11}\text{Cl}$ and varying amounts of Na are determined. $\text{C}_5\text{H}_{11}\text{Na}$ and $\text{C}_5\text{H}_{10}\text{Na}_2$ are formed quantitatively after addition of only a little $\text{C}_5\text{H}_{11}\text{Cl}$ to Na. C_5H_{12} is formed only by interaction of $\text{C}_5\text{H}_{11}\text{Na}$ with $\text{C}_5\text{H}_{11}\text{Cl}$ and not by dimerisation of free radicals. Simultaneous formation of olefines and alkanes is doubtful evidence of the existence of free radicals, since dimerisation is energetically much more probable than disproportionation. Free radicals may, however, account for some of the side-reactions in Wurtz syntheses.

XVIII. More $\text{C}_5\text{H}_{10}\text{Na}_2$ is formed at 42° than at 0° , a free radical mechanism being probable. $\text{C}_5\text{H}_{11}\text{Na}$ is quantitatively removed by an excess of C_6H_6 , but $\text{C}_5\text{H}_{10}\text{Na}_2$ does not react with C_6H_6 . Small amounts of C_6H_6 react only to the extent of $\sim 50\%$ with an excess of $\text{C}_5\text{H}_{11}\text{Na}$, although Ph_2 reacts quantitatively. R. S. C.

Catalytic hydration of acetylene and some alkylacetylenes. R. E. SOHAAD and V. N. IPATIEV (J. Amer. Chem. Soc., 1940, 62, 178—180).—Passage of C_2H_2 and H_2O with or without C_2H_4 or $\text{C}_2\text{H}_4\text{-N}_2$ over a solid H_3PO_4 catalyst at $260\text{--}300^{\circ}/1\text{ atm.}$ gives MeCHO . At $150\text{--}204^{\circ}$ $\text{CH}_2\cdot\text{CHMe}$ and H_2O give COMe_2 ; $\Delta^{\alpha}\text{-C}_4\text{H}_{10}$ gives similarly COMeEt , Δ^{α} - or $\Delta^{\beta}\text{-C}_5\text{H}_{10}$ gives COMePr^{a} , $\Delta^{\alpha}\text{-C}_6\text{H}_{12}$ gives COMeBu^{a} , and $\Delta^{\alpha}\text{-C}_7\text{H}_{14}$ gives COPr^{a_2} . Some (?) $\Delta^{\beta}\text{-C}_4\text{H}_{10}$ accompanies the COMeEt . This and the formation of COPr^{a_2} indicate that isomerisation accompanies or precedes hydration. In all cases condensation products are also formed. R. S. C.

Photochemical formation of trichlorobromomethane from chloroform and bromine.—See A., 1940, I, 124.

Action of fluorine on organic compounds. VI. Vapour-phase reaction between ethane and fluorine in progressively varying proportions. J. D. CALFEE, N. FUKUIARA, and L. A. BIGELOW (J. Amer. Chem. Soc., 1939, 61, 3552—3554; cf. A., 1938, II, 131).—Passage of C_2H_6 and F_2 over Cu gauze (cf. Calfee *et al.*, A., 1937, II, 479) gives CF_4 and C_2F_6 . Azeotropic mixtures, $\sim 2:1\text{ C}_2\text{H}_6\text{-C}_2\text{F}_6$, b.p. -92° , and $\sim 6:1:1\text{ C}_2\text{H}_6\text{-C}_2\text{F}_6\text{-SiF}_4$, b.p. -92° , are also obtained. C_2H_6 and CHF_3 give an azeotropic mixture, b.p. -96° . R. S. C.

Halogenation of hydrocarbons. Substitution of chlorine and bromine into straight-chain olefines.—See B., 1940, 114.

Structure of vinyl polymerides. VI. Polyvinyl halides. C. S. MARVEL, J. H. SAMPLE, and M. F. ROY. **VII.** Polyacrylyl chloride. C. S. MARVEL and C. L. LEVESQUE (J. Amer. Chem. Soc., 1939, 61, 3241—3244, 3244—3246; cf. A., 1940, II, 4).—**VI.** Polyvinyl halides are shown to be $[\text{CH}_2\cdot\text{CHHal}\cdot\text{CH}_2\cdot\text{CHHal}]_x$ (cf. A., 1930, 1402). The chloride (I) in dioxan loses only a little Cl to Zn, giving an insol., cross-linked product, but in very dil. solution loses 84—87% of its Cl, giving a product (II), sol. in dioxan, probably of the type, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot$ (cf. Flory, A., 1939, II, 401). The bromide (III) similarly loses 85.9% of the Br. Ozonisation and subsequent hydrolysis and oxidation of (II) gives no $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, obtained thus from polybutadiene. HNO_3 is without effect on (II), and Cl_2 causes addition and substitution. I is not liberated from KI in peroxide-free dioxan by (I) or (III). In "cellosolve," (I) loses HCl to KOH, giving an insol., reddish-brown polymeride, (?) $[\text{CH}\cdot\text{CH}]_n$ (n is very large). The absorption spectrum of (I) resembles that of $\text{CH}_2(\text{CHMeCl})_2$, but not that of $\text{CHMeCl}\cdot\text{CHEtCl}$.

VII. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COCl}$ in POCl_3 or SOCl_2 is polymerised to a pale yellow solid by ultra-violet light and in POCl_3 also by Bz_2O_2 . The photo-polymerised product is entirely (or nearly so) $[\text{CH}_2\cdot\text{CH}(\text{COCl})\cdot\text{CH}(\text{COCl})\cdot\text{CH}_2]_x$, because with Br in POCl_3 it gives 30% of a bromide, the Me ester from which liberates 40% of I from KI in dioxan and thus contains mainly units of type $\text{CBr}(\text{CO}_2\text{Me})\cdot\text{CBr}(\text{CO}_2\text{Me})$. Polymerised methylacrylyl chloride does not react with Br. R. S. C.

Photochemistry of di-iodoacetylene and tetra-iodoethylene.—See A., 1940, I, 124.

Synthesis of methyl alcohol from carbon dioxide and hydrogen.—See B., 1940, 114.

Preparation of pure *n*-octyl alcohol.—See B., 1940, 114.

Aldehyde-nitroparaffin condensations. B. M. VANDERBILT and H. B. HASS (Ind. Eng. Chem., 1940, 32, 34—38).—The conditions for the prep. of a NO_2 -alcohol from a NO_2 -paraffin and an aldehyde are described and discussed. The following are prepared in

EtOH with NaOH as catalyst by the general reaction $\text{CHRR}'\text{NO}_2 + \text{R}''\text{CHO} \rightarrow \text{NO}_2\cdot\text{CHRR}'\cdot\text{CHR}''\cdot\text{OH}$: β -nitropropanol, b.p. $99^\circ/10$ mm., γ -nitrobutan- β -ol, b.p. $92^\circ/10$ mm. (acetate, b.p. $103^\circ/10$ mm.), β -nitrohexan- γ -ol, b.p. $108^\circ/10$ mm., β -nitrobutanol, b.p. $105^\circ/10$ mm. (acetate, b.p. $103^\circ/10$ mm.), γ -nitropentan- β -ol, b.p. $100^\circ/10$ mm., γ -nitroheptan- δ -ol, b.p. $115^\circ/10$ mm., β -nitro- β -methylpropanol, m.p. $89.5-90^\circ$, γ -nitro- γ -methylbutan- β -ol, b.p. $90^\circ/10$ mm., β -nitro- β -methylhexan- γ -ol, b.p. $109^\circ/10$ mm., β -nitropentanol, b.p. $117^\circ/10$ mm., γ -nitrohexan- β -ol, b.p. $112^\circ/10$ mm., ϵ -nitrooctan- δ -ol, b.p. $124^\circ/10$ mm., β -nitro- β -methylbutanol, b.p. $98^\circ/10$ mm. (acetate, b.p. $109^\circ/10$ mm.), γ -nitro- γ -methylpentan- β -ol, b.p. $100^\circ/10$ mm., γ -nitro- γ -methylheptan- δ -ol, b.p. $119^\circ/10$ mm., β -nitro- γ -methylbutanol, b.p. $111^\circ/10$ mm., γ -nitro- δ -methylpentan- β -ol, b.p. $96-98^\circ/10$ mm., γ -nitro- β -methylpentan- δ -ol, b.p. $111^\circ/10$ mm. (stereoisomeride, b.p. $121^\circ/10$ mm., m.p. 53°). Interaction of the appropriate NO_2 -paraffin with CH_2O (2 mols.) yields the following: β -nitro- β -methylpropane- $\alpha\gamma$ -diol, m.p. $149-150^\circ$, β -nitro- β -ethylpropane- $\alpha\gamma$ -diol, m.p. 56° (diacetate, b.p. $157^\circ/10$ mm.), β -nitro- β -propylpropane- $\alpha\gamma$ -diol, m.p. $81-81.5^\circ$, and β -nitro- β -isopropylpropane- $\alpha\gamma$ -diol, m.p. $87-88^\circ$. Hydrogenation (Raney Ni) of the nitroglycols yields β -amino- β -methyl-, m.p. $108-109^\circ$, β -ethyl-, m.p. $37.5-38.5^\circ$, β -propyl-, m.p. 58° , and β -isopropylpropane- $\alpha\gamma$ -diol, m.p. 74° . The potential industrial importance of the NO_2 -alcohols and the NH_2 -alcohols is stressed.

J. D. R.

Kinetics of polyesterification. Effects of mol. wt. and viscosity on reaction rate.—See A., 1940, I, 120.

3-Nitrophthalates of ethylene and diethylene glycol monoethers. A. J. VERAGUTH and H. DIEHL (J. Amer. Chem. Soc., 1940, 62, 233).—The Me, Et, Bu, and Ph ethers of $(\text{CH}_2\text{OH})_2$ are identified by conversion by 3:1:2- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{CO}_2)_2\text{O}$ at $>150^\circ$ (in PhMe, if necessary) into the *H* 3-nitrophthalates, m.p. $128.4-129^\circ$, (anhyd.) $118-118.6^\circ$ or $(+\text{H}_2\text{O})$ $94.2-94.5^\circ$, $121-120.6^\circ$ (?), and $112-113^\circ$, respectively. Diethylene glycol Me ether *H* 3-nitrophthalate has m.p. $(+\text{H}_2\text{O})$ $87-90^\circ$ and (anhyd.) $91.4-92.2^\circ$, but the corresponding Et and Bu ether esters and the ethylene glycol ClH_2Ph ether ester are oils.

R. S. C.

Production of $\beta\gamma$ -butylene glycol by fermentation.—See A., 1940, III, 168.

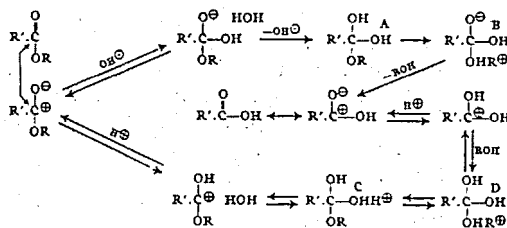
Alkyl peroxides. XII. Ethylidene diperoxide. XIII. Tripropylidene triperoxide. A. RIECHE and R. MEISTER (Ber., 1939, 72, [B], 1933-1938, 1938-1940).—XII. H_2O_2 and MeCHO (1:1) are converted by P_2O_5 in Et_2O at 0° essentially into dimeric butylene ozonide, $\text{O}\langle\text{CHMe}\cdot\text{O}_2\cdot\text{CHMe}\rangle\text{O}$, which is "cracked" at 70° /diminished pressure giving permonoparacetaldehyde, $\text{CHMe}\langle\text{O}\cdot\text{CHMe}\rangle\text{O}_2$, b.p. $40-45^\circ/14$ mm., and, at 80° , ethylidene peroxide (I), $\text{CHMe}\langle\text{O}_2\rangle\text{CHMe}$, m.p. 63° , which is readily volatile at room temp. Its ring structure appears to be confirmed by its comparative resistance to hydrolysing

agents. It is not appreciably affected by prolonged contact with warm H_2O or with 25% H_3PO_4 at 100° . Its oxidising action is very small. Iodometric determination in EtOH indicates 2.7% active O (theory 26.7%) whilst TiCl_3 indicates only 1%. The 6-membered ring appears very stable to chemical reagents and, when divided, more prone to intramol. evolution of O_2 than to formation of AcOH .

XIII. Prolonged treatment with P_2O_5 of an equimol. mixture of H_2O_2 and EtCHO in Et_2O at $0-5^\circ$ gives, after removal of Et_2O and warming in a vac., the liquid, very explosive tripropylidene triperoxide (II), $\text{CHEt}\langle\text{O}_2\cdot\text{CHEt}\rangle\text{O}_2$, the constitution of which is supported by the at. refraction and the parachor. It is not so resistant as (I) to hydrolysis but a complete conversion into EtCHO and H_2O_2 appears impossible. The iodometric method shows only about half of the expected H_2O_2 . Under the influence of alkali about 75% of (IV) is transformed into EtCO_2H . H. W.

Hydrogen exchange reactions of esters in relation to reactivity in condensation reactions.—See A., 1940, I, 121.

Mechanism of ester hydrolysis and ester formation. O. MUMM (Ber., 1939, 72, [B], 1874-1878).—The following schemes are advanced for the alkaline and acid hydrolysis:



The inverse scheme is representative of ester formation. Confirmation is found in the behaviour of carboxylic esters of pyridonemethide during alkaline hydrolysis and of ethylallyl ethers of Me *o*-hydroxytoluate. H. W.

Recognition of carboxylic acids as ureides with aid of carbodi-imides. V. F. ZETZSCHE and A. FREDRICH (Ber., 1939, 72, [B], 1735-1740; cf. A., 1939, II, 467).—Under the conditions used for the production of ureides from aromatic carbodi-imides (use of Et_2O , C_6H_6 , COMe_2 , light petroleum, or cyclohexane as solvent or without solvent at room temp.) carbodicyclohexylimide (I) gives almost exclusively anhydrides, particularly with fatty acids. By the use of higher temp. and of $\text{C}_5\text{H}_5\text{N}$ or alcohols as solvents the ureide production becomes in some cases the main reaction. Benzoyl-, m.p. $160-161^\circ$, stearyl-, m.p. $73-75^\circ$, and butyryl-, m.p. $144-145^\circ$, dicyclohexylcarbamide are described. The displacement of the anhydride to the ureide formation in alcohols and bases inhibits an approx. quant. prep. of esters and substituted amides from carboxylic acid (1 mol.) and (I) (1 mol.) in presence of alcohols or amines. The sparing solubility of dicyclohexylcarbamide permits a ready detection of free carboxylic acids in acid anhydrides. (I) can also be applied to the almost complete removal of acids from anhydrides. H. W.

Catalyst for production of acetic acid from acetylene.—See B., 1940, 114.

Preparation of acetyl bromide. T. M. BURTON and E. F. DEGERING (J. Amer. Chem. Soc., 1940, **62**, 227).—Addition of 99.5% AcOH to PBr_3 (prepared in 99.5% yield by adding Br to red P) gives 71.4–73.4% of AcBr , much HBr being evolved. Addition of PBr_3 to boiling Ac_2O (excess) gives 81.7% of AcBr with evolution of HBr . R. S. C.

Thermal decomposition of acetyl iodide.—See A., 1940, I, 120.

Chlorination of butyl trichloroacetates. H. M. WADDLE and H. ADKINS (J. Amer. Chem. Soc., 1939, **61**, 3361–3364).—Passage of Cl_2 (2 mols.) into $\text{CCl}_3\cdot\text{CO}_2\text{Bu}^a$ (510 g.), b.p. 100–101°/24 mm., illuminated by a W lamp, gives β - (158–175), b.p. 94–96°/5 mm., and δ -chloro-*n*-butyl trichloroacetate (50 g.), b.p. 127–131°/5 mm. $\text{CCl}_3\cdot\text{CO}_2\text{Bu}^b$ (510 g.), b.p. 93–94°/24 mm., gives similarly β - (I) (118–122), b.p. 80–81°/5 mm., and γ -chloroisobutyl (139), b.p. 98–99°/5 mm., and $\alpha\alpha$ -dichloroisobutyl trichloroacetate (41–56 g.), b.p. 101–105°/5 mm. $\text{CCl}_3\cdot\text{CO}_2\text{Bu}^{\text{sec}}$ (508 g.), b.p. 88–89°/19 mm., gives β -chloro- α -methyl-*n*-propyl (II) (137–144), b.p. 83–84°/5 mm., α -chloro-methyl-*n*-propyl (or, less probably, γ -chloro- α -methyl-*n*-propyl) trichloroacetate (21–37 g.), b.p. 108–110°/5 mm. By hydrolysis with 10% NaOH at <35° are obtained β - (III), b.p. 74–76°/25 mm. (phenylurethane, m.p. 52.5–53.5°), and δ -chloro-*n*-butan- α -ol, b.p. 72–75°/10 mm. (phenylurethane, m.p. 54–55°), γ -chloroisobutyl alcohol, b.p. 76–78°/21 mm. (phenylurethane, m.p. 63.5–64°), (? α -)chloro-*n*-butan- β -ol, b.p. 56°/12 mm. (phenylurethane, m.p. 78.5–79°), and $\alpha\alpha$ -dichloro-*n*-butan- α -ol, b.p. 87–93°/6 mm., but (I) gives Pr^bCHO and (II) gives only a little $(\text{CHMe})_2$. Structures are assigned from physical consts. and by conversion of (III) into $\text{CH}_2\text{EtCl}\cdot\text{CH}_2\text{Cl}$, b.p. 127°, by $\text{SOCl}_2\text{-C}_6\text{H}_5\text{N}$. R. S. C.

Preparation of tricaprylin. E. B. HERSHBERG (J. Amer. Chem. Soc., 1939, **61**, 3587–3588).—Simultaneous addition of purified *n*- $\text{C}_{17}\text{H}_{35}\cdot\text{COCl}$ (kept in excess) and aq. NaOH or KOH to glycerol at –5° to 0° gives 84–89% of trioctoin, f.p. 9.8–10.1°, b.p. 233–233.5°/1 mm. R. S. C.

Transformations of organic compounds in the solid state (compounds with long chains). II. *n*-Tricosanoic acid. R. KOHLHASS and C. STÜBER (Ber., 1939, **72**, [B], 1962–1969).—Two modifications of *n*-tricosanoic acid crystallise from COMe_2 as a mixture of which the relative proportions are not determined. Both modifications have the rhomboid form with distinct angles. The β -form is partly unstable and passes at 59.3° into the α -form (I), which separates from the molten material. (I) supports the theory of von Schoon (A., 1938, I, 348) of the formation of polymorphous modifications in aliphatic compounds with long chains. H. W.

Preparation of $\alpha\beta$ -diglycerides of fatty acids. B. F. DAUBERT and C. G. KING (J. Amer. Chem. Soc., 1939, **61**, 3328–3330).—Na α -glyceroxide and $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{COCl}$ in C_6H_6 give α -carbobenzyloxyglycerol, an oil, which with *n*- $\text{C}_{15}\text{H}_{31}\cdot\text{COCl}$ in quinoline at

room temp. gives α -carbobenzyloxyglyceryl $\alpha'\beta$ -dipalmitate, m.p. 71°, reduced by H_2 -Pd-black in abs. EtOH at 2 atm. to PhMe and $\alpha\beta$ -dipalmitin (I), m.p. 64°. Similarly are obtained α -carbobenzyloxyglyceryl $\alpha'\beta$ -dimyristate, m.p. 67–68°, and α -dibenzoate, dimyristin, m.p. 59°, and, with difficulty, glyceryl $\alpha\beta$ -dibenzoate (II), m.p. 98° (p-bromobenzoate, m.p. 107°). Migration of acyl occurs when (I), but not (II), is kept in 0.025–0.1N-HCl- or $\text{-NH}_3\text{-EtOH}$. Solubilities of these and some other esters are recorded. R. S. C.

Preparation of pure stearic acid. J. P. KASS and L. S. KEYSER (J. Amer. Chem. Soc., 1940, **62**, 230).—Pure stearic acid, m.p. 69.6–70.2° (corr.), is readily prepared by hydrogenating (PtO_2) pure elaidic, α - or β -elaeostearic, or linoleic acid in AcOH at room temp./3 atm. R. S. C.

Ricinus communis. I. Oxidation of ricinoleic acid. ST. E. BRADY (J. Amer. Chem. Soc., 1939, **61**, 3464–3467).—Ricinoleic acid, m.p. \sim 5°, and its Et ester, b.p. 193–194°/2 mm. (acetate, b.p. 196°/2–3 mm.), of theoretical I val. are prepared from castor oil. With KMnO_4 in COMe_2 , the ester gives hexoic, heptoic, octoic, β -hydroxynonoic, azelaic, suberic, and an acid, m.p. 96°. With KMnO_4 -KOH in H_2O , the acid gives approx. equal amounts of the trihydroxystearic acids, m.p. (I) 110° and (II) 141°, but ricinelaic acid gives much more (I) than (II). HIO_4 oxidises (I) and (II) to β -hydroxynonaldehyde and aldehydoazelaic acid. R. S. C.

ψ -Elaeostearic acid. J. P. KASS and G. O. BURR (J. Amer. Chem. Soc., 1939, **61**, 3292–3294).— ψ -Elaeostearic acid, m.p. 77–79° (uncorr.) (Me ester, m.p. 41°), is prepared by heating linseed oil fatty acids with KOH, best in BuOH or $(\text{CH}_2\text{OH})_2$. It is hydrogenated (PtO_2 ; AcOH) at 3 atm. to stearic acid and with KMnO_4 in COMe_2 gives sebamic acid, $\text{H}_2\text{C}_2\text{O}_4$, and PrCO_2H . It is thus $\Delta^{12,13}$ -octadecatrienoic acid. It readily forms a tetrabromide, m.p. 104–104.5°, but the hexabromide, m.p. 152.5°, is smoothly obtained only in ultra-violet light. With maleic anhydride in N_2 at 145°, it gives a mixed adduct, sinters at 75°, m.p. 77°, clear at 82°, and is thus the *trans-trans-trans*- or *trans-cis-trans*-compound. The absorption spectrum accords with the triple conjugation. R. S. C.

Ether-like compounds. VI. Constitutive factors in the acid hydrolysis of esters of aliphatic carboxylic acids. E. J. SALMI (Ber., 1939, **72**, [B], 1767–1777; cf. A., 1939, II, 316).—The acid hydrolysis of $\text{CH}_2(\text{OEt})_2$, $\text{CHMe}(\text{OEt})_2$, and $\text{OEt}\cdot\text{CH}_2\cdot\text{OAc}$ has been studied. The characteristics of the normal ester hydrolysis of esters appear to be the temp. coeff. of the rate of hydrolysis and an almost const. influence of the alcohol component on the rate of hydrolysis. With ether-like hydrolysing esters, acetal-like compounds and normal esters the ratio $k_{35}:k_{25}$ is \sim 4, \sim 3.2, and 2.5–2.3, respectively. The const. action of the alcohol component is established by observations of the rate of hydrolysis of a series of Me, Et, and Pr^b esters of fatty acids and their derivatives. An anomalous behaviour appears to be shown by esters of which the acidic components are either the first homologues of different acid series

(HCO_2H ; $\text{H}_2\text{C}_2\text{O}_4$) or have strongly negative substituents in the α position ($\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$; $\text{CHCl}_2\cdot\text{CO}_2\text{H}$). Carbonic esters are also abnormal. A distant substituent has only a very weakened influence on the rate of hydrolysis. O at $\text{C}_{(\alpha)}$ appears to act not as an actual substituent but as a prolongation of the chain. At $\text{C}_{(\beta)}$ it diminishes considerably the rate of hydrolysis, OH and OAlk having almost the same effect. It appears that the position of a substituent is much more important in the influence on the rate of hydrolysis than is its individual character. In the γ position the negating substituent can be altered without greatly influencing the rate of hydrolysis; the latter is almost unchanged by entry of a substituent at $\text{C}_{(\delta)}$. Branching of the chain is not of importance unless it occurs in vicinal positions to CO_2H on the acyl or alkyl side. Branching in the chain of the alkyl of α -alkoxy-groups has no profound influence. A double linking on the acyl side has a distinct influence only if in the $\alpha\beta$ position. If several substituents are present in the acyl group it appears possible that their influence is exerted almost independently of one another. H. W.

Cleavage of unsaturated fatty acids. C. Y. HSING and K. J. CHANG (J. Amer. Chem. Soc., 1939, 61, 3589).—0- α -Dihydroxyoctadecanoic acid (from oleic acid) and $\text{Pb}(\text{OAc})_4$ in AcOH give 85% (as semicarbazone) each of $n\text{-C}_8\text{H}_{17}\cdot\text{CHO}$ and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_6\cdot\text{CHO}$ (I). 0- α -Trihydroxyoctadecanoic acid (from ricinoleic acid, m.p. 111–112°) gives similarly ~90% of the semicarbazone of (I) and a product, m.p. 112–113°. R. S. C.

Pyrolysis of diglycollic anhydride. C. D. HURD and H. G. GLASS (J. Amer. Chem. Soc., 1939, 61, 3490–3491).—At 450° diglycollic anhydride (prep. from diglycollic acid described) gives 71% of $(\text{CH}\cdot\text{CO})_2\text{O}$, much CO , and smaller amounts of CO_2 , H_2 , and unsaturated gases. In a run at 500° 4% of keten was isolated. R. S. C.

Condensations brought about by bases. VII. **Acylation of ethyl isobutyrylisobutyrate.** Cyclisation of a $\beta\delta$ -diketo-ester by sodium triphenylmethyl. B. E. HUDSON, jun., and C. R. HAUSER (J. Amer. Chem. Soc., 1939, 61, 3567–3570; cf. A., 1939, II, 262).— $\text{COPr}^t\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ (I) is formed in 55% yield by adding CPh_3Na to $\text{Pr}^t\text{CO}_2\text{Et}$ in Et_2O or in 72% yield from $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Mg in Et_2O . In the former prep., (I) is obtained as its enolate, since addition of Pr^tCOCl to the crude reaction mixture gives 42% of *Et* $\beta\delta$ -diketo- $\alpha\alpha\gamma\gamma$ -pentamethyl-*n*-heptolate (II), b.p. 137–138° (corr.)/15 mm., whereas Pr^tCOCl does not react with isolated (II), unless CPh_3Na is previously added. Adding CPh_3Na and then AcCl to (I) in Et_2O gives 52% of *Et* $\beta\delta$ -diketo- $\alpha\alpha\gamma\gamma$ -tetramethyl-*n*-hexoate (III), b.p. 122–124° (corr.)/15 mm. NaOEt is useless for these condensations. NaOEt cleaves (II) to $\text{Pr}^t\text{CO}_2\text{Et}$, but CPh_3Na in Et_2O leads to hexamethylphloroglucinol. Only oils are obtained from (III) by either reagent. R. S. C.

Gradual decomposition by oxidation of fatty acids into their next lower homologues. H. MENDEL and J. COOPS (Rec. trav. chim., 1939, 58, 1133–1143).—Fatty acids are converted into the

α -Br- and then α -OH-acid, which is oxidised [air + $\text{Pb}(\text{OAc})_4$], through the aldehyde, to the lower homologous acid (yield ~84%). Thus, palmitic acid gives successively α -bromopalmityl bromide, Me α -bromo-, α -acetoxy-, and α -hydroxy-palmitate, and α -hydroxypalmitic acid, converted by air and $\text{Pb}(\text{OAc})_4$ in C_6H_6 into $\text{Me}\cdot[\text{CH}_2]_{13}\cdot\text{CO}_2\text{H}$. Similarly, stearic acid gives α -Br- and then α -OH-acid, m.p. 91°, oxidised (at 50°) to margaric acid, m.p. 60–86°. A. T. P.

Oil from seeds of *Ongokea klaineana*, Pierre.

A. CASTILLE (Annalen, 1939, 543, 104–110; cf. Steger *et al.*, B., 1937, 1080; Boekennoogen, *ibid.*, 1233).—The oil, extracted with COMe_2 and Et_2O , has d_{20}^{20} 0.9826, n_D^{20} 1.5079, sap. val. 191.4, Ac val. 67, I val. (Wijs) $\frac{1}{2}$ hr.) 143, CNS val. (24 hr.) 64, Margosches val. (1 hr.) 187, acid val. 3.8, and contains 3.27% of unsaponifiable matter (A); it gives hexoic, octoic, lauric, palmitic, stearic, arachidic, oleic (trace), and *erythro*genic acid (II), $\text{C}_{18}\text{H}_{36}\text{O}_2$, m.p. 39.5° (separated as Et_2O -sol. Pb salt). Catalytic reduction (Pt-black or PtO_2) of (II) affords (I). Ozonolysis of the Et ester of (II) gives CH_2O , $\text{H}_2\text{C}_2\text{O}_4$, adipic acid (III), and Et H azelate; (II) is, therefore, *octadec- Δ^7 -ene- Δ^6 -* or *- Δ^6 -di-inenoic acid*. Irradiation of (II) in a high vac. or O_2 -free atm. affords a red substance (composition unchanged) which is insol. in the usual neutral, acidic, or alkaline solvents. Oxidation (KMnO_4) of (II) (as Na salt) yields *cyanogenic acid*, $\text{C}_{17}\text{H}_{33}(\text{OH})_2\cdot\text{CO}_2\text{H}$, m.p. 92°, which when irradiated in absence of air turns blue [this gives a colourless EtOH -solution which deposits a red compound (composition unchanged), now insol.]. (A) contains an alcohol, m.p. 328° (acetate, m.p. 192.5°), phytosterol, stigmasterol, and deca- Δ^7 -ene- Δ^7 - or Δ^7 -di-inene (IV), b.p. 209°/763 mm. [*Hg* compound, oxidised (O_3) to CH_2O , HCO_2H , $\text{H}_2\text{C}_2\text{O}_4$, and (III)], which is reduced to $n\text{-C}_{10}\text{H}_{22}$. (IV) may arise from (II). H. B.

Diketen: a new industrial chemical. A. B. BOESE (Ind. Eng. Chem., 1940, 32, 16–22).—The historical development of diketen, $\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}\text{CO}$

(I), and its structural formula are discussed, and the known reactions are reviewed with emphasis on the potential industrial application of many products (e.g., $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{NHPh}$, etc.). The following new applications of (I) are described. $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{OH}$ and (I) with PhSO_3H yield β -ethoxy-ethyl acetate, b.p. 93–94°/3 mm., in 84% yield. $(\text{CH}_2\cdot\text{NH}_2)_2$ in H_2O with (I) gives *NN'*-diacetoacetyl-ethylenediamine, m.p. 168–169°, in 72% yield. *o*-Tolidine in $\text{C}_2\text{H}_4\text{Cl}_2$ with (I) gives a 93% yield of *NN'*-diacetoacetyl-*o*-tolidine, m.p. 206–207°. $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ and (I) in H_2O yield 80% of 1-sulphophenyl-3-methyl-5-pyrazolone. C_6H_6 with (I) and AlCl_3 gives CH_2BzAc in 73% yield. (I) is polymerised by *tert.* bases in inert solvents to dehydroacetic acid, and is depolymerised by pyrolysis at 550–600° to keten. The potential industrial importance of keten as an acetylating agent and as a synthetic agent is stressed, and many examples are given.

J. D. R.

Electrolytic dissociation of dicarboxylic acids in water and in aqueous alkali chloride solutions.—See A., 1940, I, 116.

Action of diazonium salts with ascorbic acid; general reaction of dienols. R. WEIDENHAGEN and H. WEGNER [with K. H. LUNG and L. NORDSTRÖM] (Ber., 1939, 72, [B], 2010—2020).—Ascorbic acid (I) and p -C₆H₄Me·N₂·SO₄H in H₂O at room temp. rapidly give p -tolylhydrazido-oxalyl-1-threonolactone (II),

$\text{CH}_2\text{--}\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CH}(\text{OH}) \end{array}\text{--CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, m.p. 175—176° (decomp.), $[\alpha]_D^{20} + 59.1^\circ$ in EtOH, hydrolysed by gently boiling H₂O to oxal- p -tolylhydrazide (III), m.p. 153° (decomp.), and l -threonic acid, identified as the phenylhydrazide, m.p. 158°, $[\alpha]_D^{20} + 57.2^\circ$ in EtOH, and as dibenzoyl-1-threonolactone, m.p. 114°, $[\alpha]_D^{20} + 174.4^\circ$ in EtOH. Fission of (II) by NHPH·NH₂ in EtOH leads to oxalphenyltolylidihydrazide, m.p. 252—253° (decomp.). (I) and the requisite diazotised amine afford phenylhydrazido-, m.p. 155—157° (decomp.), $[\alpha]_D^{20} + 63.8^\circ$ in EtOH, and 2:5-dichlorophenylhydrazido-, m.p. 110° (decomp.), $[\alpha]_D^{20} + 84.4^\circ$ in EtOH, -oxalyl-1-threonolactone. In a similar manner isoascorbic acid yields p -tolylhydrazido-oxalyl-d-erythronolactone, m.p. 117° (decomp.), $[\alpha]_D^{20} - 62.8^\circ$ in EtOH, hydrolysed by boiling H₂O to (III) and d-erythronolactone, m.p. 104—105°, $[\alpha]_D^{20} - 73.2^\circ$ in H₂O. Hydroxytetrionic acid affords p -tolylhydrazido-oxalylglycollic acid, m.p. 184—185° (decomp.), which is hydrolysed to (III) and glycollic acid. Reductive acid yields β -ketoglutar- p -tolylhydrazide, m.p. 157° (decomp.) [semicarbazone, m.p. 207° (decomp.)]. Reductone and diazotised 2:5:1-C₆H₃Cl₂·NH₂ give glyoxyl-2:5-dichlorophenylhydrazide (hydrate), m.p. 125—126° [phenylhydrazone, m.p. 223° (decomp.)]. H. W.

Catalyst for production of acetaldehyde from acetylene.—See B., 1940, 114.

Chain length and chain-ending processes in acetaldehyde decomposition.—See A., 1940, I, 120.

Crotonaldehyde condensation. Reaction of crotonaldehyde with formamide. H. L. DU MONT and W. SCHMIDT (Ber., 1939, 72, [B], 2029—2035).—Crotonaldehyde (I), HCO·NH₂, and NaHCO₃ at 100° give a resin, C₁₄H₁₇O₃N, converted by p -C₆H₄Me·SO₂Cl and C₅H₅N into a compound, C₂₁H₂₃O₅NS, and by p -C₆H₄Br·NH·NH₂ into the substance, C₂₈H₃₁O₄N₃Br. (I), HCO·NH₂, CuCO₃, and U₃O₈ in dioxan at 100° give a resin with 5.38% N. Gradual addition of (I) to HCO·NH₂ containing anhyd. ZnCl₂ at 100° gives NH₂·CO₂·NH₄, a little aldehydocolloidine (II), and, after treatment of the products sol. and insol. in H₂O with HCl, the hydrochlorides, C₁₅H₂₄O₃N₂Cl₂ and C₁₀H₁₆ONCl (whence the base, C₁₀H₁₅ON). (I), HCO·NH₂, and anhyd. AlCl₃ at 75° give small amounts of (II) a resin (III) with 6.95% N which is sol. in H₂O and an insol. resin which with p -C₆H₄Me·SO₂Cl gives the compound, (C₈H₁₂ON)₉SO₂·C₆H₄Me; from another resin fraction a compound, C₁₄H₂₄O₂N₂Br₂, is obtained by Br—EtOH. A portion of (III) which cannot be pptd. from H₂O by NaOH yields to CHCl₃ a substance, C₂₀H₂₃O₂N₃. Aq. NH₃ and (I) at 100° afford the material, C₈H₁₂ON. HCO·NH₂, (I), and CdCl₂ in dioxan at 100° yield the

material, C₁₂H₁₇ON. HCO·NH₂, (I), and piperidine give a resin free from N and insol. in HCl. H. W.

Hydroxyaldehydes. III. Preparation of δ -methoxyvaleraldehyde. R. PUMMERER and M. SCHÖNAMSGRUBER (Ber., 1939, 72, [B], 1834—1843).—Successive treatment of CH₂(CH₂OH)₂ with Na and MeI affords γ -methoxypropan- α -ol (I), b.p. 150—150.5°/738 mm., 76—78°/18 mm., which is converted by anthraquinone-2-carboxyl chloride into γ -methoxypropyl anthraquinone-2-carboxylate, m.p. 132° (corr.). PBr₃ and C₅H₅N convert (I) into γ -methoxypropyl bromide (II), b.p. 29—30°/15 mm., 129.5—131°/736 mm., which is transformed by C₆H₄(CO)₂NK at 190° into trimethylenedipthalimide, m.p. 202° (corr.). Mg allyl bromide and (II) in Et₂O give a brominated product which after treatment with boiling C₆H₅N yields α -methoxy- Δ^6 -hexene, b.p. 124°/742 mm., which is ozonised in AcOH at 0° and then reduced by Zn dust to δ -methoxyvaleraldehyde (III), b.p. 59°/14.5 mm. [Me₂ acetal (IV), b.p. 77—78°/15 mm.], which immediately gives all the typical aldehyde reactions and almost certainly is present in the open form. Attempted purification of (III) through the H sulphite appears to be accompanied by an aldol condensation (due to conc. alkali used) leading to δ -methoxy- α - ω -methoxypentenylvaleraldehyde, b.p. 152°/14 mm. (decomp.). Treatment of (III) or (IV) with boiling 2N-H₂SO₄ under N₂ leads to very slight increase in acidity and gives unchanged material, aldol, and compounds of higher b.p. which have not been investigated. OH·[CH₂]₅·OH (V) is oxidised by cold, alkaline KMnO₄ to glutaric acid in 80% yield. Gradual addition of (V) to PCl₅ in CCl₄ affords Cl·[CH₂]₅·Cl, b.p. 76—78°/21 mm., which is converted into the corresponding dinitrile and thence into pimelic acid, m.p. 104° (corr.). The diurethane of (V) has m.p. 176° (corr.). Pentane- $\alpha\epsilon$ -diyl dianthraquinone-2-carboxylate, m.p. 218.5° (corr.), is described. (V) is transformed by Na and MeI into ϵ -methoxypentan- α -ol (VI), b.p. 95°/17 mm., 98.5°/20 mm., which does not yield a cryst. urethane or H phthalate but gives 2-methoxypentan- α -yl anthraquinone-2-carboxylate, m.p. 88° (corr.). (VI) is oxidised by K₂Cr₂O₇ and H₂SO₄ to (III). H. W.

Keten and its dimeride. C. D. HURD and A. S. ROE (J. Amer. Chem. Soc., 1939, 61, 3355—3359).—In presence of a trace of H₂SO₄ or p -C₆H₄Me·SO₃H, keten and PhOH, Bu^oOH, or CMe₂Et·OH at room temp. give ~90% of the derived acetate. With CH₂O, acraldehyde, crotonaldehyde, or HCO₂Me at 20° or -80°, keten gives polymeric oils, probably (RCO·OAc)_x, in which R is unsaturated. Keten and anhyd. HCO₂H give formic acetic anhydride, b.p. 33—33.5°, which with NH₂Ph gives readily and only NHPH·CHO, thus establishing the order of electron-attraction, Ph > Me > H, from the fission of asymmetric acid anhydrides. PbEt₄ does not react with keten. The keten dimeride (I) is a resonance hybrid of COMe·CH:CO and β -crotonolactone. Its redetermined parachor is 188.0. It is 23% enolised (MgPr⁶Br; C₃H₈ and only a trace of C₃H₆ formed). It is depolymerised at 650°, but much gas is also formed. With PhCHO and KOAc, it gives CHPh·CH·COMe and CO₂ by way of

OH-CHPh·C(COMe)·CO and CHPh·C(COMe)·CO₂H. With PbEt₄ it gives an unstable, yellow solid.

R. S. C.

Hydrogenation of a higher ketone with catalysts consisting mainly of copper, cobalt, and cerium under atmospheric pressure. K. KINO and S. KATO (J. Soc. Chem. Ind. Japan, 1939, 42, 362B).—A higher ketone, prepared from commercial stearic acid, gave the corresponding sec. alcohol with H₂ in 8 hr. at 150°/atm. pressure in presence of Cu-Co, Co-Ni, and Ni-Ca, whereas Cu, Cu-Zn, Cu-Ag, Cu-Cr, Cu-Ce, Cu-Ca, Co, Ce, and Ni-KOH were unsuitable.

T. F. W.

Preparation of a higher secondary alcohol from a higher ketone by hydrogenation under pressures of 5 and 20 atmospheres. K. KINO and S. KATO (J. Soc. Chem. Ind. Japan, 1939, 42, 363B).—A higher ketone, prepared from commercial stearic acid, gave the corresponding sec. alcohol with H₂ at 150°/5 atm. in presence of Co-Ni, Cu-Co, and Ni-Ca. Under 20 atm. Co-Zn, Cu-Co, Cu-Ce, Co-Ni, Co-Cu, and Ni-Ca were effective.

T. F. W.

Hydrogenation of $\alpha\gamma$ -diketones to ketols. P. S. STUTSMAN and H. ADKINS (J. Amer. Chem. Soc., 1939, 61, 3303—3306).—Hydrogenation of COR·CH₂·COMe in MeOH using 0.9—1.0 H₂ at 100°/100—200 atm. in presence of Raney Ni gives the following yields of COR·CH₂·CHMe·OH (A): R = Me 35, Et 51, Pr^a 58, Pr^b 50, Bu^a 66, Bu^b 49, CHMeEt 64% (cf. Sprague, A., 1935, 198). Yields are approx. the same in Et₂O, dioxan, or EtOH, but are 4—20% higher using 1 mol. of H₂ diluted with N₂. The structure of (A) is determined by distilling with H₂C₂O₄ and reducing the olefine by H₂—Raney Ni at 30—40°/100 atm. to CORPr^a, identified by solid derivatives. No OH·CHR·CH₂·COMe is formed. Further hydrogenation (Ni) at 100—125°/100 atm. in MeOH gives OH·CHR·CH₂·CHMe·OH (R = Et 92, Pr^a = Bu^a 94, CHMeEt 80%). 27% of fission of CPh·CHEt·COMe (cf. *loc. cit.*) to PhCHO and COMePr^a occurs during hydrogenation and is due to hydrogenolysis and not to disproportionation of the ketol, since COBu^a·CH₂·CHMe·OH is stable in Et₂O at 60° in presence of Raney Ni. The following are described. *n*-Hexan- γ -on- ϵ -ol, b.p. 75—78°/12 mm.; *n*-pentan- β -on- δ -ol, b.p. 93—95°/43 mm.; *n*-heptan- δ -on- β -ol, b.p. 101°/24 mm.; β -methyl-*n*-hexan- γ -on- ϵ -ol, b.p. 72—73°/9 mm.; *n*-octan- δ -on- β -ol, b.p. 91°/8 mm.; ζ -methyl-*n*-heptan- δ -on- β -ol, b.p. 86°/9 mm. (*phenylhydrazone*, m.p. 111—113°); $\beta\beta$ -dimethyl-*n*-hexan- γ -on- ϵ -ol, b.p. 72—74°/10 mm.; ϵ -methyl-*n*-heptan- δ -on- β -ol, b.p. 113—114°/36 mm.; Δ^8 -*n*-hexen- γ -one, b.p. 136—139°/740 mm. (2:4-dinitrophenylhydrazone, m.p. 164—165°); β -methyl- Δ^8 -*n*-hexen- γ -one, b.p. 147—148.5°/739 mm. (2:4-dinitrophenylhydrazone, m.p. 140—141°); Δ^8 -*n*-hepten- δ -one, b.p. 156—162°/740 mm. (2:4-dinitrophenylhydrazone, m.p. 142—143°); Δ^8 -*n*-octen- δ -one, b.p. 178°/740 mm. (2:4-dinitrophenylhydrazone, m.p. 108—109°); ζ -methyl-, b.p. 163—170°/741 mm. (2:4-dinitrophenylhydrazone, m.p. 101—101.5°), and ϵ -methyl- Δ^8 -*n*-hepten- δ -one, b.p. 170°/741 mm.; $\beta\beta$ -dimethyl- Δ^8 -*n*-hexen- γ -one, b.p. 153—154°/740 mm. (2:4-dinitrophenylhydrazone, m.p. 135—135.5°); γ -methyl-*n*-heptan- δ -one, b.p.

152—154°/740 mm. (*semicarbazone*, m.p. 106—107°); *n*-heptan- $\beta\delta$ -diol, b.p. 107—108°/8 mm. (*bisphenylurethane*, m.p. 101—101.5°); *n*-octan- $\beta\delta$ -diol, b.p. 117—118°/8 mm. (*bisphenylurethane*, m.p. 126—127°); ϵ -methyl-*n*-heptan- $\beta\delta$ -diol, b.p. 111—112°/8 mm. (*bisphenylurethane*, m.p. 129—130°); ϵ -methyl-*n*-hexan-, m.p. 134—135°, and ζ -methyl-*n*-heptan-, m.p. 143—143.5°, $\beta\delta$ -diol *bisphenylurethane*.

R. S. C.

Oxidation of aldoses by hypiodite. V. K. MYRBÄCK (Svensk Kem. Tidskr., 1939, 51, 206—217; cf. A., 1939, I, 615).—With pure aldose solutions there is no advantage in using alkali carbonate solutions and some sugars cannot be determined in this way. A method is proposed in which the oxidation always goes to completion. If the glucose is mixed with ketoses, sucrose, or similar compounds the methods of Auerbach and Bodländer and others may be used unless appreciable quantities of substances which react with I are present. Traces of COMe₂ can completely invalidate the results.

T. H. G.

Oxidation of glucosides by lead tetra-acetate in aqueous solution. J. M. GROSHEINTZ (J. Amer. Chem. Soc., 1939, 61, 3379—3381; cf. A., 1940, II, 3).—Oxidation of α - and β -methyl-*l*-arabinopyranoside by aq. Pb(OAc)₄ proceeds exactly as with HIO₄ (Jackson *et al.*, A., 1937, II, 325), except that the HCO₂H formed is further oxidised to CO₂, consuming a third mol. of oxidant.

R. S. C.

Synthesis of 5:6-dimethylglucose. M. R. SALMON and G. POWELL (J. Amer. Chem. Soc., 1939, 61, 3507—3510).—Diisopropylideneglucose and CH₂Ph·O·CH₂Cl with Na in Et₂O at room temp. or KOH in boiling Et₂O give 3-benzoyloxymethyl-diisopropylideneglucose, b.p. 157—160°/0.15 mm., hydrolysed by ~90% AcOH to 3-benzoyloxymethylmonoisopropylideneglucose, an oil [*di*(phenylurethane), m.p. 148—148.5°], which with Me₂SO₄·NaOH (twice) gives 5:6-dimethyl-3-benzoyloxymethylisopropylideneglucose, b.p. 155—163°/0.12 mm. Na-EtOH then gives 5:6-dimethylisopropylideneglucose, m.p. 56—56.5°, [α]_D²⁰ −12.8° in H₂O (*phenylurethane*, m.p. 88—89°; ? NN'-*diphenylallophanate*, m.p. 241—242°) (with PhMe and MeOH), hydrolysed by *n*-HCl at 80° to 5:6-dimethylglucose (I), hygroscopic, [α]_D²⁰ +4.0±0.3° in H₂O [*p*-bromophenylosazone, m.p. 155.5—156° (decomp.)], which reduces Fehling's solution or KMnO₄ in the cold and gives Schiff's reaction. The structure of (I) is proved by oxidation (HIO₄; Br) to dimethylglyceric acid (*p*-phenyl-, m.p. 62.5—63°, and *p*-bromo-phenacyl ester, m.p. 66.5—67°). M.p. are corr.

R. S. C.

Emulsin. XLII. Fission of *d*-xylosides, *l*-xylosides, and *dl*-xylosides by sweet almond emulsin. B. HELFERICH, E. GÜNTHER, and W. W. PIGMAN (Ber., 1939, 72, [B], 1953—1959).—*l*-Xylose is converted by anhyd. NaOAc and Ac₂O at 100° into β -*d*-xylopyranose tetra-acetate, m.p. 123—125°, [α]_D²⁵ +25.3° in CHCl₃, which is converted into *phenol*- β -*l*-xylopyranoside triacetate, m.p. 143—145°, [α]_D²⁵ +50.7° in CHCl₃, de-acetylated (Zemplén) to *phenol*- β -*l*-xylopyranoside (I), m.p. 178—180°, [α]_D²⁰ +49.5° in H₂O, which slowly reduces boiling Fehling's solution.

Phenol- β -*d*-xylopyranoside (II) is hydrolysed by sweet almond emulsin, by which (I) is scarcely affected by prolonged action at high concn. Admixture of equal amounts of (I) and (II) affords *phenol*- β -*dl*-xylopyranoside, m.p. 187° (corr.), which, in solution, behaves towards emulsin as a mixture of (I) and (II). Protocatechualdehyde-4- β -*d*-glucopyranoside tetra-acetate, acetobromo-*l*-xylose, and NaOH in aq. COMe₂ at room temp. afford *protocatechualdehyde*-4- β -*d*-glucoside-3- β -*l*-xyloside *hepta*-acetate, m.p. 148—150°, $[\alpha]_D^{20} + 9.4^\circ$ in CHCl₃, deacetylated (NaOMe in MeOH) to *protocatechualdehyde*-4- β -*d*-glucoside-3- β -*l*-xyloside (III), m.p. 235—237°, $[\alpha]_D^{20} - 32.7^\circ$ in H₂O. *Protocatechualdehyde*-4- β -*d*-glucoside-3- β -*d*-xyloside (IV) (+EtOH), softens at ~72°, solvent-free, m.p. 128—130°, $[\alpha]_D^{20} - 89.8^\circ$ in H₂O, and its *hepta*-acetate, m.p. 147—149°, $[\alpha]_D^{20} - 69.9^\circ$ in CHCl₃, are described. Hydrolysis of (IV) by emulsin occurs at about the same rate as that of other protocatechualdehydedynglycosides, both *d*-glucose and β -*d*-xylose being eliminated. Hydrolysis of (III) proceeds much less readily; possibly β -*l*-xylose engages the vicinal glucose much more completely than does its enantiomorph so that the enzyme approaches with greater difficulty. With the highly active enzyme the complete removal of glucose from (III) has been effected.

H. W.

Substitution reactions of oxygen atoms between glucose, fructose, and water. T. TITANI and K. GOTO (Proc. Imp. Acad. Tokyo, 1939, 15, 298—299).—The interchange of ¹⁸O between H₂¹⁸O, glucose, and fructose is determined by measurements of the *d* of the aq. solvent before and after substitution. Each sugar has one easily exchangeable O, and a mechanism is proposed involving opening the lactone ring by addition of H₂¹⁸O followed by ring closure by fission of H₂O.

J. D. R.

Synthesis of oligosaccharides in the mannose series. D. D. REYNOLDS and W. L. EVANS (J. Amer. Chem. Soc., 1940, 92, 66—69).— β -*D*-Mannose 6-CPh₃ ether 1:2:3:4-tetra-acetate (prepared in improved yield by shaking mannose and CPh₃Cl in C₅H₅N at 50° and then with Ac₂O at room temp.), m.p. 204—206°, and HBr-AcOH at 0° give rapidly β -*d*-mannose 1:2:3:4-tetra-acetate, m.p. 135.5—136.5°, which with acetobromogentiobiose (I), Ag₂O, and drierite in CHCl₃ give 6- β -gentiobiosido- β -*d*-mannose *hendeca*-acetate, m.p. 122—123°, $[\alpha]_D^{20} - 21.02^\circ$ in CHCl₃, and, in one experiment, *Et* gentiobiose *hepta*-acetate (II), m.p. 158—159°, $[\alpha]_D^{20} - 23.06^\circ$ in CHCl₃, also obtained from (I) and EtOH as above. α -*d*-Mannose 6-CPh₃ ether 1:2:3:4-tetra-acetate (prep. described), m.p. 123—124°, $[\alpha]_D^{20} + 73.5^\circ$ in CHCl₃, and HBr-AcOH give α -*d*-mannose 1:2:3:4-tetra-acetate, converted by acetobromoglucose etc. into 6- β -*d*-glucosido- α -*d*-mannose octa-acetate, $[\alpha]_D^{20} + 26.01^\circ$ in CHCl₃. Hudson's rules are valid for 6-but not for 4-linked mannose derivatives and for (II). M.p. are corr.

R. S. C.

Reduction products of *d*-glucoheptulose. F. L. HUMOLLER, S. J. KUMAN, and F. H. SNYDER (J. Amer. Chem. Soc., 1939, 61, 3370—3374).—*d*-Glucoheptulose (improved prep.) and Na-Hg give β -*d*- and α -glucoheptitol (I). (I) was previously termed

α -*d*-glucoheptitol (Khouvine *et al.*, A., 1933, 373), as it is isolated with $[\alpha]_D^{20} + 2.04^\circ$ in H₂O due to an impurity; its nature is proved by its yielding pure (I) when heated with 10% H₂SO₄, giving only the hepta-acetate and (CPh₃)₂ ether of (I), and by studies of solubility.

R. S. C.

Partly methylated disaccharides. II. Maltose. K. HESS and W. GRAMBERG (Ber., 1939, 22, [B], 1898—1908; cf. A., 1937, II, 276).—Benzylidene- β -benzylmaltoside is best methylated in small portions and with a large excess of Ag₂O to benzylidene-2:3:6:8:9-pentamethyl- β -benzylmaltoside, new m.p. 140°, hydrolysed by 0.004N-HCl-MeOH to 2:3:6:8:9-pentamethyl- β -benzylmaltoside (I), m.p. 109.5—110.5°, $[\alpha]_D^{20} + 35.3^\circ$ in MeOH, +49.9° in CHCl₃, +40.2° in COMe₂; more conc. acid causes fission of the maltose union. This is converted by Ac₂O-C₅H₅N at 20° into its 10:12-*di*acetate, m.p. 85—86°, $[\alpha]_D^{20} + 29.5^\circ$ in MeOH, +40.9° in CHCl₃, +41.5° in C₆H₆, and by BzCl-C₅H₅N at 115° into its 10:12-*di*benzoate, m.p. 146.5°, $[\alpha]_D^{20} + 51.7^\circ$ in C₆H₆, +68.8° in CHCl₃, +48.5° in COMe₂. (I) and CPh₃Cl afford 12-*triphenylmethyl*-2:3:6:8:9-pentamethyl- β -benzylmaltoside (II) (purified by sublimation in a vac.), m.p. 70—80°, $[\alpha]_D^{20} + 39.2^\circ$ in MeOH, +35.5° in CHCl₃, +33.6° in C₆H₆, reconverted by HCl-AcOH into (I). (II) is esterified by CH₂Ph-COCl-C₅H₅N and is transformed by BzCl-C₅H₅N into 12-*triphenylmethyl*-2:3:6:8:9-pentamethyl- β -benzylmaltoside 10-*benzoate* (III), m.p. (indef.), 70—80°, $[\alpha]_D^{20} + 42.7^\circ$ in MeOH, +52.3° in CHCl₃, +31.9° in C₆H₆, converted by NaOMe in boiling MeOH into (I). Attempts to bring (II) into reaction with *p*-C₆H₄Me-SO₂Cl were unsuccessful. HCl-AcOH converts (III) into 2:3:6:8:9-pentamethyl- β -benzylmaltoside *benzoate*, which with Ag₂O-MeI affords non-cryst. 2:3:6:8:9:10-hexamethyl- β -benzylmaltoside 12-*benzoate* (III), $[\alpha]_D^{20} + 31.8^\circ$ in MeOH, +39.5° in CHCl₃, +22.2° in C₆H₆. Successive treatments with NaOMe-MeOH at 60° and warm 5% HCl transform (III) into 2:3:6-trimethylbenzylglucoside and 2:3:4-trimethylglucose, $[\alpha]_D^{20} + 59.7^\circ$ in MeOH, +62.4° in H₂O.

H. W.

Partly methylated disaccharides. III. Cellobiose. K. HESS and H. L. KWANG (Ber., 1939, 72, [B], 1906—1908).—12-*Triphenylmethyl*-2:3:6:8:9-pentamethyl- β -benzylcellobioside, a liquid, $[\alpha]_D^{20} - 17.74^\circ$ in COMe₂, -36.21° in C₆H₆, -25.99° in CHCl₃, -16.74° in MeOH, obtained from benzylidene- β -benzylcellobioside and MeI-Ag₂O, does not react with *p*-C₆H₄Me-SO₂Cl but is transformed by BzCl in C₅H₅N at 100° into 12-*triphenylmethyl*-2:3:6:8:9-pentamethyl- β -benzylcellobioside 10-*benzoate*, a glass, $[\alpha]_D^{20} - 18.3^\circ$ in COMe₂, -19.9° in C₆H₆, -13.2° in CHCl₃, -17.4° in MeOH. This is hydrolysed by HCl-AcOH at 10° to non-cryst. 2:3:6:8:9-pentamethyl- β -benzylcellobioside 12-*benzoate*, $[\alpha]_D^{20} - 28.9^\circ$ in COMe₂, -41.1° in C₆H₆, -35.2° in CHCl₃, -32.4° in MeOH, which with Ag₂O-MeI at ~60° affords 2:3:6:8:9:10-hexamethyl- β -benzylcellobioside 12-*benzoate* (I), $[\alpha]_D^{20} - 39^\circ$ in COMe₂, -42° in C₆H₆, -30.2° in CHCl₃, -33.8° in MeOH. (I) is hydrolysed by NaOMe-MeOH followed by 5% HCl to 2:3:4-trimethylglucose and trimethyl- β -benzylglucoside.

2:3:6:8:9-Pentamethyl- β -benzylcellobioside 10:12-dibenzoate has $[\alpha]_D^{20}$ -27.7° in COMe_2 , -47.7° in C_6H_6 , -31.5° in CHCl_3 , -34.2° in MeOH . H. W.

Preparation of N-glycosides of aniline and substituted anilines. F. WEYGAND (Ber., 1939, 72, [B], 1663—1667; cf. Kuhn and Weygand, A., 1937, II, 233).—A mixture of sugar (1 mol.), amine (1.1—1.4 mols.), and H_2O (2.4 mols.) when heated at 100° with good stirring becomes homogeneous after 2—15 min. according to the components used. After short further heating a solvent suitable for crystallisation is added and the mixture is allowed to cool, whereby the glycoside separates in 44—99% yield. Further purification is usually unnecessary. The products are stable in the absence of acid vapours and are best preserved in the presence of a small amount of gaseous NH_3 . The following are described: aniline, m.p. 140° (tetra-acetate, m.p. 149°), *o*-toluidine-, m.p. $97-98^\circ$, *p*-toluidine-, m.p. $112-113^\circ$ (tetra-acetate, m.p. $143-144^\circ$), and *p*-phenetidine-, m.p. $115-116^\circ$ (tetra-acetate, m.p. 132°), *-d*-glucoside; aniline-, m.p. 144° , *p*-toluidine-, m.p. $154-155^\circ$, $[\alpha]_D^{20}$ -49.5° to $+10.5^\circ$ in aq. EtOH, and *p*-phenetidine-, m.p. 140° , *-d*-galactoside; aniline-, m.p. $180-181^\circ$ (decomp.), and *p*-toluidine-, m.p. $183-184^\circ$, *-d*-mannoside; aniline-, m.p. $140-141^\circ$, and *p*-toluidine-, m.p. $124-125^\circ$, $[\alpha]_D^{20}$ -41.5° in $\text{C}_5\text{H}_5\text{N}$, *-d*-xyloside. H. W.

Constitution of polyoses of wood. E. HUSEMANN (Naturwiss., 1939, 27, 595).—Osmotic measurements show that in xylans from wheat straw and beechwood, mannan from spruce, arabogalactan from larch, and cellulose from beech, the degrees of polymerisation of the pentose (xylose, arabinose) and hexose (mannose, galactose) units are approx. 150, 160, 220 and <1500 , respectively. The particles which produce osmotic pressure are mols. (90% of the xylan mols. are of the same size), not mol. aggregates, and they retain their degree of polymerisation when converted into acyl derivatives. Measurements of $\eta_{\text{sp.}}$ of solutions of the polymerides show that the mols. of mannan and the xylans form long straight chains whilst those of arabogalactan form chains with many branches. W. McC.

Macromolecular compounds. CCXXVII. Cellulose. LIII. Normal and faulty celluloses. H. STAUDINGER and A. W. SOHN (Ber., 1939, 72, [B], 1709—1717).—Nitration of a series of cellulose types, chiefly of technical origin, leads to products of mean degree of polymerisation exceeding that of the initial material. Polymeric analogous compounds are obtained from cellulose (I) which has been reprecipitated from Schweitzer's solution. It is considered that normal (I) mols. consist of an unbroken chain of glucose residues with ester-like union at the end of the normal chains. These linkings are disrupted by dissolution in Schweitzer's reagent and in these solutions only the chains of the normal (I) mol. are dissolved. When treated with HNO_3 the ester linkings remain intact and hence the degree of polymerisation of the nitrate exceeds that of (I). Ester-like linkings between individual thread mols. can be established in many ways, e.g., by boiling $(\text{COCl})_2$, and the nitrates

of such "oxalylcelluloses" are more complex than those of the initial (I). Treatment with oxidising agents causes oxidative degradation and the glucose residues of the (I) chain undergo chemical change. The no. of CO_2H in oxycellulose exceeds that in (I) and CO is also present. Such oxidative attack can lead to the alteration of a glucose residue in such a manner that a carbonic ester is formed. These products are readily hydrolysed by alkali or NH_3 with production of "faulty celluloses." The linkings are stable towards nitrating acid so that polymeric-analogous nitrates do not appear to be produced. "Faulty celluloses" therefore contain interspersed foreign groups and the ester group no. = mean degree of polymerisation of the nitrates in COMe_2 /mean degree of polymerisation of the cellulose in Schweitzer's reagent -1 . The importance of the ester group no. for the behaviour of textiles is discussed. H. W.

Unesterified (A) primary, (B) secondary, hydroxyl [groups] in acetone-soluble cellulose. (A) F. B. CRAMER and C. B. PURVES. (B) F. B. CRAMER, R. C. HOCKETT, and C. B. PURVES (J. Amer. Chem. Soc., 1939, 61, 3458—3462, 3463—3464).—(A) Interaction of commercial, COMe_2 -sol. cellulose acetate (0.56—0.67 free OH per glucose unit) with *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at 20° is at first rapid and then slow, passing through a max. due to very slow replacement of RSO_2 by Cl. Hydrolysis of the product caused decomp. or loss of RSO_2 , but $\text{NaI}-\text{COMe}_2$ leads to replacement of 0.197 RSO_2 by I, indicating that 35% of the OH are primary. This figure is a min., as some OH are not accounted for. $\text{C}_5\text{H}_5\text{N}, \text{HCl}$ in $\text{C}_5\text{H}_5\text{N}$ at 100° causes replacement of 0.24 RSO_2 by Cl, indicating that 43% of the OH are primary (cf. Sakurada *et al.*, A., 1935, 201). If the *p*- $\text{C}_6\text{H}_4\text{MeSO}_2$ derivative is isolated after the rapid reaction is ended, the product contained 0.19 RSO_2 , of which 84—90% are primary (NaI). It follows that the COMe_2 -sol. acetate prepared by partial hydrolysis of the triacetate contains much free primary and sec. OH, but that in the COMe_2 -insol. product of similar Ac content, prepared by direct, partial acetylation, the primary OH are preferentially acetylated. The 6-position of the I in iodocellulose (unstable to the usual reagents) is confirmed by conversion by a Zn—Cu couple in AcOH at 100° into a deoxycellulose acetate, which, when distilled with aq. acid, gives methylfurfuraldehyde and with 2% $\text{HCl}-\text{MeOH}$ etc. gives isorhamnose (isolated as tetraacetate). All, except the degraded, products have unchanged mol. wt. (η).

(B) Cellulose acetate containing 0.67 free OH per glucose unit should contain 1 $\text{OH}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ in 20—32 glucose units, if the distribution of free OH is purely random. This is not the case in such a commercial COMe_2 -sol. acetate, for oxidation by $\text{Pb}(\text{OAc})_4$ in 50% CHCl_3 —AcOH indicates one free glycol unit in 100—150 glucose units. Cellulose triacetate is stable to $\text{Pb}(\text{OAc})_4$. R. S. C.

Preparation of primary amines. A. GALAT and (Miss) G. ELION (J. Amer. Chem. Soc., 1939, 61, 3585—3586).—Good yields of primary amines are obtained by adding 1 mol. of RCl or RBr to NaI and

$(\text{CH}_2)_6\text{N}_4$ (1 mol. each) in hot 95% EtOH and keeping the mixture at room temp. for up to several weeks.

R. S. C

β -Aminobutane, di-*sec*.-butylamine, *n*-butyl-*sec*.-butylamine, and their preparation in optically active state. (MLLE.) A. FLEURY-LARSONNEAU (Bull. Soc. chim., 1939, [v], 6, 1576—1582).—Hydrogenation (Ni or, better, Raney Ni + NH_3 -MeOH) of COMeEt gives CHMeEt·NH₂ (I) and some (CHMeEt)₂NH (II) (cf. Mignonac, A., 1921, i, 165). (I) affords, through the *d*- and *l*-H tartrates (*r*-tartaric acid reduces amount of *l*-acid necessary), *d*- (III), $[\alpha]_D +7.4^\circ$ in H₂O, and *l*-*sec*.-butylamine, $[\alpha]_D -5.0^\circ$ in H₂O (cf. Thomé, A., 1903, i, 321), respectively. (I) and CHMeEtBr or BuBr in EtOH give (II) or NHBu·CHMeEt (IV) (picrate, m.p. 105°), respectively; (III) similarly gives *d*-(II), $[\alpha]_D +23.6^\circ$, or *d*-(IV), $[\alpha]_D +16.1^\circ$, respectively.

A. T. P.

Complex thioarsenates.—See A., 1940, I, 128.

Complex phosphodecatungstates.—See A., 1940, I, 127.

Aliphatic polyamines. X. J. VAN ALPHEN (Rec. trav. chim., 1940, 59, 31—40; cf. A., 1939, II, 301).— $(\text{CH}_2\text{NH}_2)_2\cdot\text{H}_2\text{O}$ (I) and α , γ -dibromohexane (II) in EtOH-KOH give mainly α , γ -di-(β -aminoethylamino)hexane (III), b.p. 212°/25 mm. (tetrapicrate, m.p. 213°; tetranitrate, +H₂O; tetraphenyl-carbamyl, m.p. $\sim 216^\circ$, and thiocarbamyl derivative, +2EtOH, m.p. ~ 125 — 135°), some α , π -di-(β -aminoethylamino)- η κ:10-diaza-hexadecane, m.p. 32°, b.p. 314—323°/23 mm. (hexaphenyl-carbamyl, m.p. 100—120°, and thiocarbamyl derivative, m.p. ~ 90 — 120°), and some higher amines, together with a little 1-(β -aminoethyl)-1-azacycloheptane, b.p. 212° [picrate, m.p. 200°; phenyl-carbamyl (picrate, m.p. 183°) and thiocarbamyl derivative, m.p. 93°], obtained in better yield from very dil. EtOH solutions of (I) + (II) after 3 months. Only straight-chain non-cyclic amines are formed; thus NH₂ reacts much more quickly than NH. (III) and CS₂-EtOH give a thiocarbamate, converted at 140° into α , γ -di-1'-(2'-thiotetrahydroiminazolo)hexane, m.p. 216°. α , γ -Di-(β -benzylaminoethylamino)hexane (tetrahydrochloride, decomp. 255°) and PhCHO give α , γ -di-1'-(2'-phenyl-3'-benzyltetrahydroiminazolo)hexane, m.p. 128°.

A. T. P.

***N*-Acetylphenyl- α -*d*-glucosaminide, m.p. 241—243°, $[\alpha]_D +203^\circ$ in H₂O, +233° in EtOH.**—See A., 1940, III, 164.

Synthesis of α -amino-acids by means of alkyl-acetoacetic esters. I. V. V. FEOFILAKTOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 755—758; cf. A., 1939, II, 364).—PhN₂·OK and CHRAc·CO₂Et (I) in the cold give probably NPh·N·CRAc·CO₂Et, hydrolysed by aq. EtOH-alkali to NHPH·N·CR·CO₂H (II), which is reduced by Zn-EtOH-HCl at 0° to NH₂·CHR·CO₂H. Thus, (I) (R = CHMeEt) affords (II) (R = CHMeEt), reduced to a mixture of isoleucine, m.p. 286°, and *allo*isoleucine, m.p. 275—276° (all m.p. in sealed tubes). (I) (R = Bu ^{β}) gives the phenylhydrazone, forms, m.p. 114° and 144°, of Bu ^{β} CO·CO₂H, converted into leucine, m.p. 292—293°.

[With E. V. VINOGRADOVA.] (I) (R = CH₂Ph) affords phenylalanine (Cu salt, +2H₂O).

[With V. N. ZAITZEVA.] (I) (R = Me) gives (II) (R = Me) and thence alanine.

A. T. P.

Synthesis of amino-acids from benzamidomalonic ester. E. P. PAINTER (J. Amer. Chem. Soc., 1940, 62, 232—233).—NHBz·CH(CO₂Et)₂ (simplified prep.) and RI in abs. EtOH give products, hydrolysed to α -NH₂-acids by const.-boiling HCl or HBr. Glycine (85% yield), norleucine, OPh·[CH₂]₂·CH(NH₂)·CO₂H, and OH·[CH₂]₂·CH(NH₂)·CO₂H (as lactone) are thus prepared. Attempts to prepare β - and γ -halogeno- α -amino-acids gave impure products (cf. Redemann *et al.*, A., 1939, II, 495).

R. S. C.

Mercury compounds as catalysts of the synthesis of aspartic acid from fumaric acid and ammonia. T. ENKVIST [with, in part, L. LAASONEN] (Ber., 1939, 72, [B], 1927—1932).—The addition of NH₃ to fumaric acid (I) is followed by observing the increase in NH₂-N [determination by Van Slyke's nitrite process after removal of NH₄-N by evaporation with Ca(OH)₂] or the diminution in KMnO₄ consumption in H₂SO₄ at $\sim 55^\circ$. Very little or no catalytic action is exerted by Cl₂, Br, I, FeSO₄, PbO, KCr(SO₄)₂, or FeCl₃ in presence of Seignette salt (NH₂-N process) or by CoSO₄, Ni(NO₃)₂, [Co(NH₃)₄CO₃]₂SO₄, CuSO₄, CdCl₂, PdCl₂, H₂PtCl₆, Pb(NO₃)₂, MnCl₂, or KHCO₃ (KMnO₄ process). HgO, HgCl₂, and HgSO₄ cause marked acceleration. A distinct but less marked action is exerted by AgNO₃. Addition of piperidine, NHEt₃, C₅H₅N, or CN·CH₂·CO·NH₂ does not enhance the action of HgCl₂. Replacement of NH₃ by (NH₄)₂CO₃ diminishes the yield of aspartic acid. Hg salts accelerate only in the measure in which they pass into Hg^{II} salts. NaOH in presence or absence of Hg^{II} salts has a restrictive influence. HgCl₂, MnCl₂, or I in absence of ascorbic acid does not influence the rate of addition of NH₃ to maleic acid. The catalytic action appears due to the formation of an unstable complex from (I) and the Hg salt.

H. W.

Polymeric products from amino-acids. Y. Go and H. TANI (Bull. Chem. Soc. Japan, 1939, 14, 510—516).—*l*-Alanine in *n*-NaOH with ClCO₂Me yields carbomethoxy-*l*-alanine (a syrup), which with SOCl₂ yields *l*-alaninecarboxylic anhydride, m.p. 92° (decomp.). Similarly from *l*-leucine are prepared carbomethoxy-*l*-leucine, m.p. 52°, and *l*-leucinecarboxylic anhydride, m.p. 77—78° (decomp.). Polymerisation of glycinecarboxylic anhydride in H₂O vapour or in C₅H₅N at 100° yields polyglycines (mol. wt. 1044—5775) which are unattacked by enzymes and show identical X-ray diagrams. The X-ray diagrams of polyleucine, polyalanine, and polyglycylalanine (which are prepared as for polyglycine) are discussed; the last-named appears to be a mixture of polyglycine, polyalanine, and the true interpolymeride.

J. D. R.

Organic syntheses with sulphuryl chloride. W. W. BINKLEY [with E. F. DEGERING] (J. Amer. Chem. Soc., 1939, 61, 3250—3251).—SO₂Cl₂ (1 mol.) and NHR₂ (1 mol.), first at 0° and then boiling, or, less well, SO₂Cl₂ and NHR₂·HCl give *di*-methyl-, b.p. 66°/10 mm., -ethyl- (I), b.p. 69°/5 mm., -*n*-propyl-, b.p. 83.5°/4 mm., and -*n*-butyl-aminosulphonyl

chloride, b.p. 95–96°/3 mm., converted by boiling MeOH into the corresponding *Me sulphonates*, m.p. —, 80°, 135°, and 117°, respectively, also obtained from ClSO_3Me (2 mols.) and $\text{NHR}_2\cdot\text{HCl}$ (1 mol.) at 100°. $\text{NaOR}\cdot\text{ROH}$ and (I) in Et_2O give *Et*, b.p. 86°/5 mm., *Pr*^a, b.p. 80·5°/3 mm., and *Bu*^a *diethylaminosulphonate*, b.p. 73·5°/2·25 mm., also obtained in small yields from ClSO_3R and NHET_2 . R. S. C.

Synthesis and properties of isocysteine and isocystine. A. SCHÖBERL and H. BRAUN (Annalen, 1939, 542, 274–291; cf. Gabriel, A., 1907, i, 625; 1908, i, 181).— β -Phthalimidopropionic acid, m.p. 150–151° [from β -alanine and α - $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 160°], and Br-red P give the α -Br-derivative, m.p. 169–171° [Me ester, m.p. 103–104° (lit. 52–53°)], hydrolysed (48% HBr) to α -bromo- β -aminopropionic acid [hydrobromide (I), m.p. 188–189°; Me ester hydrochloride, m.p. 123–125° (decomp.)]. *isoSerine* [from $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ and aq. NH_3 at 100° (autoclave)] similarly affords β -phthalimido- α -hydroxypropionic acid (II), m.p. 196–197° (corr.); the Me ester (III), m.p. 106–108° (corr.) [O-acetate, m.p. 135–137° (corr.)], of (II) and PCl_5 in boiling C_6H_6 give ~50% of Me α -chloro- β -phthalimidopropionate, m.p. 119–120° (corr.), hydrolysed (20% HCl) to α -chloro- β -aminopropionic acid hydrochloride (IV), m.p. 134–135°. The monophosphoric acid ester, m.p. 188–189° (corr.), of (II) is obtained (after decomp. with H_2O) as a by-product from (III) and PCl_5 in CHCl_3 . (I) or (IV), neutralised with $\text{N}\cdot\text{NaOH}$, and Na_2S_2 in N_2 at room temp. give a product which is reduced (Sn , aq. HCl) to isocysteine (V) (hydrochloride, m.p. 137–139°) (purified through the mercaptide). Oxidation (I– H_2O) of (V) affords isocystine (VI), m.p. 185° (decomp.) (hydriodide, m.p. 189–191°).

Hydrolytic fission (mechanism: A., 1939, II, 204) of the S·S linking occurs much more readily with (VI) than with cystine or $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$. With H_2O or $\text{N}\cdot\text{H}_2\text{SO}_4$ at 100°/12 hr., (VI) give H_2S (46·4 or 34·1%, respectively) and (V) (17·5 or 25·7%, respectively); with $\text{N}\cdot\text{NaOH}$ at 100° (not at 50°) NH_3 (32·3%) is produced. (V) and (VI) can be determined colorimetrically with phosphotungstic acid (cf. A., 1938, II, 211) or polarographically (cf. Brdička, A., 1933, 681).

Constitution of peptides. II. Raman spectra and structure of amides.—See A., 1940, I, 96.

Organic catalysts for removal of carbon monoxide from formamide. II. Catalysts with alcoholic hydroxyl as active group. T. ENKVIST [with H. MERIKOSKI and P. TIKKANEN] (Ber., 1939, 72, [B], 1717–1723; cf. A., 1939, II, 249).—Substances with primary and sec. alcoholic OH [$\text{C}(\text{CH}_2\cdot\text{OH})_4$, inositol, quercitol] accelerate the removal of CO from $\text{HCO}\cdot\text{NH}_2$ if alkali is present whereas no such action is observed with *tert.* alcohols ($\text{CPh}_3\cdot\text{OH}$; pinacol) even in the presence of alkali. Common aliphatic (*n*-undecyl, sec.-octyl) or alicyclic (cyclohexanol) monohydric alcohols are not catalysts. Aromatic rings under certain conditions (cinnamyl and benzyl alcohol), $\text{NH}_2\cdot\text{N}$ (di- and tri-ethanolamine, choline and its chloride), and CO_2Na ($\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$) have feeble activating effect. CO_2Et , $\text{CO}\cdot\text{NH}_2$, and particularly $\text{CO}\cdot\text{NHAr}$ and similar groups have a more pronounced

action. Several alcoholic OH in the same mol. are mutually helpful; this is less marked with dihydric compounds (glycol and its derivatives), more marked with tri- to hexa-hydric alcohols such as glycerol, erythritol, quercitol, $\text{C}(\text{CH}_2\cdot\text{OH})_4$, mannitol, duleitol, sorbitol, and inositol, all of which have about the same effect pro OH. $\cdot\text{CHO}$ and $\cdot\text{CO}\cdot$ are very restrictive. There is no catalytic action with glucose, fructose, galactose, lactose, or maltose and only slight action of helicin. Etheral O or bridge O in glycosides or disaccharides appears indifferent or activating. A marked catalytic effect is produced by α -methyl-*d*-glucoside and salicin and, very definitely, by sucrose (I). PhOH and pyrogallol in presence of Na_2CO_3 and $\text{HCO}\cdot\text{NH}_2$ at 140° give a great evolution of gas. It is probable that (I) and phenols in presence of alkali could be used advantageously as catalysts in the technical prep. of $\text{HCO}\cdot\text{NH}_2$ from CO and NH_3 .

H. W.

Glycidamides [$\alpha\beta$ -oxidopropionamides] with hypnotic properties. Claisen-Darzen reaction. E. FOURNEAU and J. R. BILLETTER (Bull. Soc. chim., 1939, [v], 6, 1616–1625; cf. A., 1934, 396).—Me hexyl ketone and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}\cdot\text{Et}_2\text{O}\cdot\text{Na}$ (better than NaNH_2 or NaOEt) give *Et* $\alpha\beta$ -oxido- β -methyl-nonoate, b.p. 119°/0·9 mm. *Et* $\alpha\beta$ -oxido- β -methyl-hexoate (I) and NH_2Me do not react at 100°, but at 140° give α -methylamino- β -hydroxy- β -methyl-*n*-hexo-methylamide, m.p. 119° (hydrochloride, m.p. 198°). (I) and NHMe_2 -aq. MeOH at 150° give $\text{CHEt}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{NMe}_2$, b.p. 76°/30 mm. (methiodide, m.p. >300°). Glycidamides and $\text{HBr}\cdot\text{Et}_2\text{O}$ act abnormally to give ethylenic products. A. T. P.

Complex salts of thiocarhamide with lead and thallium. C. MAHR [with H. OHLE] (Annalen, 1939, 542, 44–48).— $\text{CS}(\text{NH}_2)_2$ and conc. aq. $\text{Pb}(\text{ClO}_4)_2$ containing 20% HClO_4 give the complex, $\text{Pb}(\text{ClO}_4)_2\cdot 6\text{CS}(\text{NH}_2)_2$. The complexes, $\text{Pb}(\text{ClO}_3)_2\cdot 6\text{CS}(\text{NH}_2)_2$ (prep. in neutral solution), $\text{TlClO}_4\cdot 4\text{CS}(\text{NH}_2)_2$, and $\text{TlClO}_3\cdot 4\text{CS}(\text{NH}_2)_2$ (using TlOAc and NaClO_3), are described. H. B.

α -Alkanesulphonylamides. A. POMERANTZ and R. CONNOR (J. Amer. Chem. Soc., 1939, 61, 3386–3388; cf. A., 1938, II, 86).— $\text{CHRBr}\cdot\text{CO}\cdot\text{NH}_2$, $\text{R}'\text{SH}$, and $\text{NaOEt}\cdot\text{EtOH}$, first at 0° and then at room temp., give $\text{SPR}^a\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, $\text{SBu}^a\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, ethyl-thiolacetamide, m.p. 50·5–51° (lit. 44°), α -ethyl-, m.p. 65–65·5°, α -*n*-propyl-, m.p. 56·5–57°, and α -*n*-butyl-thiolpropionamide, m.p. 60·5–61·5°, α -ethyl-, m.p. 100·5–101°, α -*n*-propyl-, m.p. 78–78·5°, and α -*n*-butyl-thiolbutyramide, m.p. 65–65·5°, α -ethyl-, m.p. 93·5–94°, α -*n*-propyl-, m.p. 95–95·5°, and α -*n*-butyl-thiolisobutyramide, m.p. 107·5–108°, α -ethyl-, m.p. 101·5–102°, α -*n*-propyl-, m.p. 98·5–99°, and α -*n*-butyl-*n*-valeramide, m.p. 64·5–65°, α -ethyl-, m.p. 111–111·5°, α -*n*-propyl-, m.p. 98·5–99°, and α -*n*-butyl-thiolisovaleramide, m.p. 75–75·5°, α -ethyl-, m.p. 84·5–85°, α -*n*-propyl-, m.p. 100·5–101°, and α -*n*-butyl-thiol-*n*-hexoamide, m.p. 86·5–87°. H_2O_2 – $\text{AcOH}\cdot\text{Ac}_2\text{O}$, first at 0° and then at room temp., then yield $\text{Bu}^a\text{SO}_2\cdot\text{CHR}\cdot\text{CO}\cdot\text{NH}_2$ ($\text{R} = \text{H}$, *Et*, and *Bu*^a), ethane-, m.p. 98·5–99°, and propane- α -sulphonylacetamide, m.p. 104–104·5°, α -ethane-, m.p. 126–126·5°, α -propane- α -, m.p. 122–122·5°, and α -butane- α -sul-

phenylpropionamide, m.p. 114—114.5°, α -*ethane*-, m.p. 168—168.5°, and α -*propane*- α' -*n*-*butyramide*, m.p. 137—137.5°, α -*ethane*-, m.p. 92.5—93°, impure α -*propane*- α' -, m.p. 99.5—100.5°, and α -*butane*- α' -*sulphonyl*-*isobutyramide*, m.p. 77.5—78°, α -*ethane*-, m.p. 117.5—118°, α -*propane*- α' -, m.p. 125—125.5°, and α -*n*-*butane*- α' -*sulphonyl*-*n*-*valeramide*, m.p. 125—125.5°, α -*ethane*-, m.p. 122—123.5°, α -*propane*- α' -, m.p. 116—117°, and α -*n*-*butane*- α' -*sulphonyl*-*isovaleramide*, m.p. 126.5—127°, α -*ethane*-, m.p. 112—112.5°, and α -*propane*- α' -*sulphonyl*-*n*-*hexoamide*, m.p. 119—119.5°. Bu^nSH , $\text{CH}_3\text{CMeCO}\cdot\text{NH}_2$, and a little piperidine in boiling EtOH give β -*n*-*butylthiolisobutyramide*, m.p. 54.5—55°. M.p. are corr. R. S. C.

Optical activity of α -bromopropionitrile. K. L. BERRY and J. M. STURTEVANT (J. Amer. Chem. Soc., 1939, **61**, 3583—3584).—According to Kirkwood's theory, $\text{CHMeBr}\cdot\text{CN}$ should have very low $[\alpha]$, since each substituent has cylindrical symmetry parallel to the valency linking. When prepared from (67.1% *l* + 32.9% *d*.) $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ by conversion into the amide and dehydration by P_2O_5 , $\text{CHMeBr}\cdot\text{CN}$ has $[\alpha]_D^{25} -5.25^\circ$, indicating (in absence of racemisation during synthesis) $[\alpha]_D^{25} -15.33^\circ$ for the pure *l*-compound. Possible causes of the discrepancy are briefly discussed. R. S. C.

Manufacture of α -cyano- α -butadiene.—See B., 1940, 191.

Unsaturated arsinocarboxylic acids. H. J. BACKER and R. P. VAN OOSTEN (Rec. trav. chim., 1940, **59**, 41—63).— $\text{CH}_2\cdot\text{CBr}\cdot\text{CO}_2\text{K}$ and K_3AsO_3 give α -*arsinoacrylic acid* (I), $\text{CH}_2\cdot\text{C}(\text{AsO}_3\text{H}_2)\cdot\text{CO}_2\text{H}$, m.p. 160° (decomp.) (cryst. data) [*Pb* and *Ba* (+12 H_2O) salts; NH_2Ph salt, decomp. $\sim 148^\circ$; *di*-*strychnine* (+6 H_2O), decomp. $\sim 250^\circ$, and *-quinine* salt (+6 H_2O) decomp. $\sim 155^\circ$]. K_3AsO_3 and α -*bromo-crotonic* (more readily) or *-isocrotonic acid* give α -*arsino-crotonic acid*, m.p. 158—160° (one form only) [*di*-*strychnine*, (+5 H_2O), decomp. $\sim 237^\circ$, and *-quinine* (+6 H_2O) salts]. β -*Chloro-crotonic* or *-isocrotonic acid* (reacts more readily) gives the tribasic β -*arsino-crotonic acid* (II), m.p. 151—152° (decomp.) [*Ba* (+8 H_2O), *Ba H* (+3 H_2O), and *Ag* salts; NH_2Ph salt, m.p. 140—141° (decomp.)]. (I) and the respective pinacol in EtOH give *dipinacol*—

$\text{CH}_2\text{C}(\text{CO}_2\text{H})\text{As}(\text{CMe}_2)_2$, m.p. 173—174°, and *di*-*cyclopentanonepinacol- α -arsinoacrylic acid*, m.p. 208—210°, respectively (cf. Englund, A., 1929, 945). (I) and α - $\text{C}_6\text{H}_4(\text{OH})_2\cdot\text{AcOH}$ give *dipyrocatechol- α -arsinoacrylic acid*, m.p. 168—170°. (II) and SO_2 in HCl (+KI) at 40° give β -*dichloroarsenocrotonic acid*, $\text{AsCl}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m.p. 88.5—89.5°, reconverted by H_2O_2 into (II). (I) and HCl give *trans*- β -*chloroacrylic acid*. (II) gives *pinacol*-, m.p. ~ 198 —200°, *dicyclo-pentanone*-, m.p. 162—162.5°, and *-hexanonepinacol*-, m.p. 233—234° (decomp.) (cryst. data), *dipyrocatechol*-, m.p. 175—176°, and *d*-*tartaric- β -arsinocrotonic acid*, decomp. $\sim 240^\circ$. (II) and $\text{H}_2\text{SO}_4\text{-NaH}_2\text{PO}_2$ at 0° afford β -*arsenodicrotonic acid*, $(\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMeAs})_2$, decomp. $\sim 193^\circ$. Vals. of dissociation consts. of arsinic-acids are recorded. Speeds of reaction of α -halogeno-crotonic and *-isocrotonic acids* and K_3AsO_3 are examined in detail. A. T. P.

Preparation of Grignard reagents from magnesium amalgams. E. G. ROCHOW (J. Amer. Chem. Soc., 1939, **61**, 3591).—Addition of a 0.1*N*. solution of MgMeCl and then of MeBr to 0.1, 0.5, or 1% Mg-Hg in purified N_2 and boiling for several hr. gives increases of 0, 4.1, and 25.3%, respectively, in the MgMeHal content and some MgMe_2 (formed from MgHal_2 and MgMeHal). R. S. C.

Stereoisomerides of dichlorodiamminoethylenediaminocobaltic ion.—See A., 1940, I, 129.

Redistribution reaction. IV. Interchange between lead triethyl chloride and radioactive lead tetraethyl. G. CALINGAERT, H. A. BEATTY, and L. HESS (J. Amer. Chem. Soc., 1939, **61**, 3300—3301; cf. A., 1940, II, 8).—When PbEt_4 containing *Ra-D* and inactive PbEt_3Cl are kept in $\text{C}_6\text{H}_6\text{-N}_2$, equilibrium is reached in <1 day at room temp., approx. equal amounts of *Ra-E* being found in each component. Interchange of Et and Cl is thus very rapid, the PbEt_3Cl being the catalyst as well as a reactant. R. S. C.

Lead tetraethyl: manufacture and uses.—See B., 1940, 114.

Investigation of spiro-pentane with cathode-ray interferences. F. ROGOWSKI (Ber., 1939, **72**, [B], 2021—2026).—Observations of electron deflexions show that the hydrocarbon C_5H_8 obtained by the action of Zn dust and EtOH on the tetrabromide of pentaerythritol (Gustavson, A., 1896, i, 669; Zelinski, A., 1913, i, 254) is a spiran $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{C} < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$ in which the two rings are composed of similar triangles placed at an angle of 90° to one another and having one point in common. The distance of the external from the central C is 1.54 Å. The H atoms appear to be arranged in pairs at the external C atoms with C—H distances of 1.08 Å. and to stand with the C at an angle of 109° 28' so that the plane formed by them and the C cuts the C triangle at right angles. A more precise location of the H is not possible by the method used. H. W.

Chlorinations with sulphuryl chloride. II. Peroxide-catalysed reaction of sulphuryl chloride with ethylenic compounds. M. S. KHARASCH and H. C. BROWN (J. Amer. Chem. Soc., 1939, **61**, 3432—3434; cf. A., 1939, II, 497).—Addition of 2 Cl to olefines by SO_2Cl_2 is catalysed by peroxides, the reaction being: $\text{R}_2\text{O}_2 \rightarrow \text{R}^\cdot$; $\text{R}^\cdot + \text{SO}_2\text{Cl}_2 \rightarrow \text{RCl} + \cdot\text{SO}_2\text{Cl}$; $\cdot\text{SO}_2\text{Cl} \rightarrow \text{SO}_2 + \text{Cl}^\cdot$; $\text{Cl}^\cdot + >\text{C}=\text{C}< \rightarrow >\text{CCl}\cdot\dot{\text{C}}<$; $>\text{CCl}\cdot\dot{\text{C}}< + \text{SO}_2\text{Cl}_2 \rightarrow >\text{CCl}\cdot\text{CCl}< + \cdot\text{SO}_2\text{Cl}$. *cyclo*Hexene, if freshly distilled, reacts moderately with SO_2Cl_2 and only after an induction period, giving the 1:2- Cl_2 -derivative; reaction is accelerated, and the induction period eliminated, by adding a little aged *cyclo*hexene, PhCHO , or *ascari-dole*, or by passing in dry air. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ [gives $\text{CHCl}(\text{CH}_2\text{Cl})_2$] behaves similarly. Pure $(\text{CHCl})_2$ does not react, but in presence of Bz_2O_2 (0.002 mol.) gives 85% of $(\text{CHCl})_2$. $(\text{CCl}_2)_2$ similarly, but slowly, gives C_2Cl_6 . Stilbene, best in presence of a peroxide, gives 45% of $\alpha\alpha'$ - and 33% of $\beta\beta'$ -dichloride. $(\text{CPh}_2)_2$ reacts in presence of peroxides or peroxide-

containing (not peroxide-free) AcOH (cf. Norris *et al.*, A., 1911, i, 31). Reaction of unsaturated acids and anhydrides is complex.

R. S. C.

Interaction of benzene with methylcyclobutene and methylenecyclobutene in the presence of sulphuric acid. V. N. IPATIEV and H. PINES (J. Amer. Chem. Soc., 1939, 61, 3374—3376).—A mixture of methylcyclobutene and methylenecyclobutene with C_6H_6 and 96% H_2SO_4 at 0—10° gives 1-phenyl-1-methylcyclobutane (I) (40%), b.p. 69°/8 mm., 209.6°/760 mm. [p-NHAc, m.p. 144°, and 2':4'-(NHAc)₂-derivative, m.p. 202°], p-di-1'-methylcyclobutylbenzene (II), m.p. 34°, b.p. 123—125°/6 mm. (and a small amount of isomerides; total yield 49%), and tri-(methylcyclobutyl)benzenes (11%), b.p. 155—182°/8 mm. 2% $KMnO_4$ at 100° and dil. HNO_3 at 135° do not affect (II), but HNO_3 at 160° gives p- $C_6H_4(CO_2H)_2$. With H_2 and Ni-kieselguhr in $n-C_5H_{12}$ at 65°/100 mm., (I) gives 1-cyclohexyl-1-methylcyclobutane, b.p. 72—73°/9 mm., 201.5°/760 mm. (converted by Pt- Al_2O_3 at 250° into a 1:1 mixture of CHPhMePr^a and CPhMe₂Et), but at 125° gives amylcyclohexane.

R. S. C.

Preparation and physical data of monoalkylbenzenes. A. W. SCHMIDT, G. HOPP, and V. SCHOELLER (Ber., 1939, 72, [B], 1893—1897).—The requisite ketone is obtained by the gradual addition of $AlCl_3$ to a solution of the necessary acid chloride in C_6H_6 . Reduction of this by Clemmensen's method is unsatisfactory but reliable results are obtained by the Kishner-Wolff process. The following alkylbenzenes have been obtained: propyl-, b.p. 47—49°/11 mm.; butyl-, b.p. 66—68°/12 mm.; amyl-, b.p. 87°/12 mm.; hexyl-, b.p. 97.5—101°/12 mm.; heptyl-, b.p. 116—118°/12 mm.; octyl-, b.p. 131—134°/12 mm.; dodecyl-, b.p. 183—185°/12 mm.; tetradecyl-, b.p. 153°/0.5 mm.; hexadecyl-, b.p. 171°/0.1 mm. Vals. for d_4^{20} , n_D^{20} , and η are recorded.

H. W.

Preparation of pure hydrocarbons for testing the physical methods in use for examination of hydrocarbon mixtures. I. H. I. WATERMAN, J. J. LEENDERTSE, and D. W. VAN KREVELEN. II. H. I. WATERMAN, J. J. LEENDERTSE, and J. F. SIRKS (J. Inst. Petroleum, 1939, 25, 801—808, 809—812; cf. B., 1939, 458).—I. In order to test the accuracy of the η -mol. wt. method for determining the elementary composition of saturated hydrocarbon mixtures, $C_8H_{17}Ph$ was prepared from $n-C_8H_{17}Cl$ and PhBr by the Würtz-Fittig reaction, and was then hydrogenated (150 kg. per sq. cm. initial pressure, 10% Ni catalyst, Ni on kieselguhr, temp. ~200°) to yield *n*-octylcyclohexane (I) and $C_{18}H_{34}$. $C_{18}H_{37}Cl$ and PhBr were similarly caused to yield octadecylcyclohexane and $C_{36}H_{74}$. *n*, *d*, and several other consts. are recorded. The results indicate that for the compounds considered the no. of rings per mol. may be derived from the *n* with an accuracy of ± 0.2 ring per mol.

II. It was considered possible that in the high-temp. hydrogenation prep. of (I) undesirable structural changes may have occurred. The hydrocarbon was therefore synthesised by condensation (Na at 60—130°) of cyclohexyl iodide and $n-C_{18}H_{37}Cl$. The resultant hydrocarbon was identical with that pre-

pared previously, thus indicating that the hydrogenation method does not produce undesirable changes.

T. C. G. T.

Nickel as catalyst for the hydrogenation of aromatic halogen compounds. C. F. WINANS (J. Amer. Chem. Soc., 1939, 61, 3564—3565).—In presence of Raney Ni (best 5% of the wt. of reagent), many aromatic halogenonitro-compounds are hydrogenated at 125—150°/20—100 atm. to halogenoamines in excellent yield. PhCl could not be hydrogenated to chlorocyclohexane, as the Cl is removed at the necessary temp. CH_2PhCl gives some CH_2Ph_2 . $CHMe:CHCl$, $CHPh:CHCl$, $(CHCl)_2$, and $(CCl_2)_2$ resist reduction. p- $C_6H_4Cl \cdot NO_2$, p- $C_6H_4Br \cdot NO_2$, and o- $C_6H_4I \cdot NO_2$ (I) give 97, 83, and 23%, respectively, of halogenoaniline, NH_2Ph being the main product from (I). 1:2:4- $C_6H_3Cl(NO_2)_2$ gives 91% of m- $C_6H_4(NH_2)_2$ even at <40°, but 2:5:1- $C_6H_3Cl_2 \cdot NO_2$ gives 97% of 2:5:1- $C_6H_3Cl_2 \cdot NH_2$, and 2:5:1- $C_6H_3Cl_2 \cdot N:CHPh$ gives 91% of 2:5:1- $C_6H_3Cl_2 \cdot NH \cdot CH_2Ph$. p- $C_6H_4Cl \cdot CN$ gives p- $C_6H_4Cl \cdot CH_2 \cdot NH_2$ 64 and $NH(CH_2 \cdot C_6H_4Cl \cdot p)_2$ 21%.

R. S. C.

Excitation of chain polymerisation by free radicals.—See A., 1940, I, 120.

Vinyl polymerides. VIII. Polystyrene and its derivatives. C. S. MARVEL and N. S. MOON (J. Amer. Chem. Soc., 1940, 62, 45—49; cf. A., 1940, II, 62).—o-Bromophenylmethylcarbinol (I) [prep. from o- $C_6H_4Br \cdot CHO$ and $MgMeCl$ (not $MgMeI$)], b.p. 108.5°/6.5 mm., $KHSO_4$, and a little quinol at 155—160°/21—30 mm. give 33% of o-bromostyrene, b.p. 65°/4 mm., polymerised at 160° or, better, 175° alone or, best, with 0.2% of Bz_2O_2 at 140—150° to a product (II), mol. wt. (η) 24,000. Na, best in boiling xylene (but not Zn in dioxan or Cu in $PhNO_2$), removes the Br from (II) without pptn. of a cross-linked polymeride or change in η ; nevertheless, ring-closure has not occurred, as no phenanthrene derivatives are obtained by Se or oxidation; reaction is probably replacement of Br by Na, particularly as carbonation gives a little acidic material. Poly-*m*- and -*p*-bromostyrene, moreover, react similarly with Na. It is thus probable that polystyrene and its derivatives are $[CHPh \cdot CH_2]_n$. It was impossible to polymerise $CH_2 \cdot CPhCl$ (III), α -acetoxystyrene [prep. by adding $CHPhMeBr$ to $AcCl$ to give β -bromo- α -phenylethyl acetate (91%), b.p. 105—107°/3 mm., and heating this with quinoline at 145—155° (34% yield)], b.p. 87.5—89.5°/3 mm. (dibromide, m.p. 93.5—94.5°), $CH_2 \cdot CPh \cdot OMe$, $CHPh:CHBr$, or $CHPh:CH \cdot OAc$. Poly- β -nitrostyrene is insol. SO_2Cl_2 converts (I) into o-bromo- α -chloroethylbenzene, b.p. 63—65°/2 mm., stable to quinoline. BF_3 converts (III) into s- $C_6H_3Ph_3$.

R. S. C.

Action of bromine on olefines. W. BOCKE-MÜLLER and R. JANSSEN (Annalen, 1939, 542, 166—184; cf. A., 1939, II, 96).—Contrary to Pfeiffer *et al.* (A., 1928, 633; 1931, 340), the coloured substances formed from Br and, e.g., $CH_2:CAR_2$ (Ar should not be p-NMe₂- C_6H_4 , since this results in the production of a meriquinonoid salt) are mol. compounds (A) and not carbenium salts (B). Formation of (A) is not connected with either addition of Br to the double linking or substitution. (A) are much more stable,

and in some cases are only formed, at low temp.; the reversible formation of (A) is often readily demonstrated by alternate cooling and warming (~room temp.) of solutions (CCl_4 , CH_2Cl_2) of the components. Analogous compounds are obtained with IBr but not with I. Production of (A) (dark green to violet) from the following is demonstrated: $(\text{C}_6\text{H}_5)_2$, tetra-*p*-bromophenyl-, $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*p*-chlorophenyl-, m.p. 179° (I) and 205° (II), $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*p*-diphenyl-, m.p. 218° (III) and 254° (IV), $\alpha\beta$ -di-*p*-chlorophenyl- $\alpha\beta$ -di-*p*-bromophenyl- (V), m.p. 232°, and β -bromo- α -di-*p*-diphenyl-ethylene (VI) [but not from the $\beta\beta$ -Br₂-derivative (VII)]. Proof of the non-production of (B) is afforded by the recovery of unchanged (III) and (IV), i.e., *cis*- and *trans*-forms, after treatment with Br in CH_2Cl_2 at -78° in red light (dark-room lamp); traces of Br-containing material are also produced. Conversely, decomp. of the carbenium perchlorate from either (III) or (IV) and HClO_4 - Ac_2O with H_2O gives the same mixture of (III) and (IV) in each case. Interconversion of (III) and (IV) occurs when solutions in CCl_4 -Br are cooled to -78° owing to the production of HBr; this adds at low temp. and subsequent warming causes elimination of HBr and isomerisation. Rearrangement can also occur during bromination (cf. Price *et al.*, A., 1939, II, 48); thus, (I) (probably *cis*) and (II) (*trans*) give (V) (probably *trans*) but no other isomeride. Bromination of tetrahydronaphthalene in CCl_4 at room temp. in diffused daylight is retarded by (III), (IV), $(\text{C}_6\text{H}_5)_2$, $(\text{CCl}_3)_2$, or $\text{CHMe}:\text{CH}:\text{CO}_2\text{H}$.

(I) and (II) are obtained from *p*- $\text{C}_6\text{H}_4\text{Cl}:\text{C}_6\text{H}_5$ and Cu powder in boiling C_6H_6 ; these with excess of Br (no solvent or in $\text{PhNO}_2 + \text{I}$ at 70–100°) afford (V). (I) and (II) are recovered almost unchanged from solutions in CH_2Cl_2 or CCl_4 -Br [kept at -78° and then evaporated at room temp. (vac.)].

p- $\text{C}_6\text{H}_4\text{Br}:\text{COCl}$, PhCl , and AlCl_3 give 4-chloro-4'-bromobenzophenone (VIII), m.p. 150°, the dichloride, m.p. 62–63° (prep. by PCl_5 in C_6H_6), of which with Cu powder in C_6H_6 affords (V). Oxidation (CrO_3 , AcOH) of (V) yields $\alpha\beta$ -di-*p*-chlorophenyl- $\alpha\beta$ -di-*p*-bromophenylethylene oxide, m.p. 257°, or (VIII). (*p*- $\text{C}_6\text{H}_4\text{Ph}$)₂: $\text{C}:\text{CH}_2$ (1 mol.) and Br (1 mol.) in CH_2Cl_2 at -10° give (after evaporation at <0°) the dibromide, which when heated in CCl_4 affords (VI) [similarly yields its dibromide, m.p. 70–80°, and thence (VII)].

H. B.

Condensations by sodium. XVII. Formation of triphenylene. A. A. MORTON, J. T. MASSENGALE, and G. M. RICHARDSON (J. Amer. Chem. Soc., 1940, 62, 126–129; cf. A., 1940, II, 62).—Small yields of *o*- $\text{C}_6\text{H}_4\text{Ph}_2$, triphenylene (I), and (*o*- $\text{C}_6\text{H}_4\text{Ph}$)₂ are obtained when PhCl , Na, and PhMe react. $\text{C}_5\text{H}_{11}\text{Na}$ under certain conditions, but never NaPh, metallates *o*- $\text{C}_6\text{H}_4\text{Ph}_2$ and Ph_2 , but no (I) is produced. As judged by absence of $\text{C}_6\text{H}_4\text{Cl}:\text{CO}_2\text{H}$ after carbonation, no $\text{C}_6\text{H}_4\text{ClNa}$ is formed from PhCl by NaPh or $\text{C}_5\text{H}_{11}\text{Na}$. Although (I) may be formed from Ph radicals, this is not so for Ph_2 , since Ph, produced from $\text{CPh}_3\text{N}_2\text{Ph}$, yields no Ph_2 .

R. S. C.

Interaction of bromine with anthracene in dioxan. C. C. PRICE and C. WEAVER (J. Amer. Chem. Soc., 1939, 61, 3360–3361).—Anthracene and

Br in dry dioxan give only 9:10-dibromoanthracene. In presence of a trace of atm. H_2O there are formed successively 9-bromo-10-anthrone and anthraquinone with evolution of much HBr, HOBr being the effective reagent (cf. Price, A., 1936, 1498).

R. S. C.

Aromatic hydrocarbons. XXIII. Melting with zinc dust; new method of reducing organic compounds. E. CLAR (Ber., 1939, 72, [B], 1645–1649).—Quinones and their derivatives are rapidly reduced by Zn dust (I) in molten $\text{NaCl}:\text{ZnCl}_2$ at 200–290°. NaCl lowers the m.p. of the ZnCl_2 which removes the oxide layer from (I). Slight humidity in ZnCl_2 is advisable since it facilitates the evolution of H_2 . The course of the reaction can usually be followed by the change in colour of the mixture. The yield of spectroscopically pure material frequently reaches 90%. Bimol. products are formed to some extent and may amount to 25% if dry ZnCl_2 in absence of NaCl is used. Aromatically combined ether-O is not removed. The following examples are cited: CH_2Ph_2 and $\text{CPh}_2:\text{CPh}_2$ from COPh_2 ; anthracene and 9:9'-dianthryl from anthraquinone; phenanthrene and 9:9'-diphenanthrylene 10:10'-oxide, m.p. 299°, from phenanthraquinone; strongly carcinogenic 3:4:8:9-dibenzpyrene, m.p. 308° (vac.), from 3:4:8:9-dibenzpyrene-5:10-quinone; 3:4:9:10-dibenzpyrene, m.p. 280°, from 3:4:9:10-dibenzpyrene-5:8-quinone; anthanthrene, m.p. 261° (vac.), from anthanthrone; violanthrene from violanthrone; isoviolanthrene from isoviolanthrone; anthrazine from indanthrene.

H. W.

Photochemical dehydrogenation of 7-dehydrocholestene. A. TOMINAGA (Bull. Chem. Soc. Japan, 1939, 14, 486–489).—7-Dehydrocholestene when irradiated (sunlight) in $\text{EtOH}:\text{C}_6\text{H}_6$ -eosin and CO_2 yields a bimol. substance, $\text{C}_{25}\text{H}_{38}$, m.p. 269–270° (corr.; decomp.) [$[\alpha]_D^{20} + 260^\circ$ in CHCl_3]. It is considered that photochemical dehydrogenation of ergosterol and related compounds does not involve C_{23} .

J. D. R.

Photo-oxidisable diphenylanthracenes with cyclic substituent at positions 1:2. L. VELLUZ (Bull. Soc. chim., 1939, [v], 6, 1541–1548; cf. A., 1936, 1499).—1:2-Benzanthraquinone and MgPhBr (500% of Mg at 30–40°) give 9:10-dihydroxy-9:10-diphenyl-9:10-dihydro-1:2-benzanthracene, new m.p. 249° (cf. Clar, A., 1930, 334). Irradiation in CS_2 of 9:10-diphenyl-1:2-benzanthracene (I), new m.p. 196°, gives the photo-oxide, decomp. at 130° to O_2 and (I). *o*-1-Tetrahydronaphthoylebenzoic acid is cyclised by 25% oleum to 1':2':3':4'-tetrahydro-2:3-, m.p. 211°, and -1:2-benzanthraquinone, m.p. 136° (block) (separation described). The latter and MgPhBr at room temp. give 9:10-dihydroxy-9:10-diphenyl-9:10-1':2':3':4'-hexahydro-1:2-benzanthrene, m.p. (anhyd.) 222° or (+ C_6H_6) 122° (cf. Cook *et al.*, A., 1936, 1247), reduced by $\text{KI}:\text{AcOH}$ to isomeric 9:10-diphenyl-1':2':3':4'-tetrahydro-1:2-benzanthracenes, m.p. 224° and 298°, respectively; both give impure photo-oxides, which lose O_2 at 130–135°.

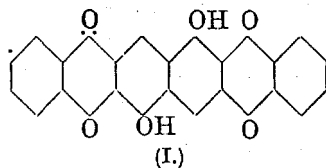
A. T. P.

Polycyclic aromatic hydrocarbons. XXI. G. M. BADGER, J. W. COOK, and F. GOULDEN (J.C.S.,

1940, 16—18).—6-Methyl-1:2-benzanthraquinone and MgMeI give 9:10-dimethoxy-6:9:10-trimethyl-9:10-dihydro-1:2-benzanthracene, m.p. 232—233.5° [9:10-(OH)₂-compound, m.p. 151—152°], which with Na affords 6:9:10-trimethyl-1:2-benzanthracene, m.p. 157—158° (picrate, m.p. 145—146°). 1:2-C₁₀H₈(CO)₂O and Mg 3-bromo-*o*-xylene (I) yield 2-(2':3'-dimethylbenzoyl)-1-naphthoic acid, m.p. 168—169° (acetoxylactone, m.p. 189—191°), which with BzCl forms 5:6-dimethyl-1:2-benzanthraquinone; this with MgMeI gives 9:10-dihydroxy-5:6:9:10-tetramethyl-9:10-dihydro-1:2-benzanthracene, m.p. 217—219°, the 9:10-(OMe)₂-derivative, m.p. 229—230°, of which with Na yields 5:6:9:10-tetramethyl-1:2-benzanthracene, m.p. 132—133° (picrate, m.p. 120—121°). *o*-C₆H₄(CO)₂O and (I) afford 2-(2':3'-dimethylbenzoyl)-benzoic acid, m.p. 126—127°, which with BzCl gives 1:2-dimethylantraquinone, reduced to 1:2-dimethylanthrane, m.p. 85.5—86°. The quinone and MgMeI in C₆H₆-Et₂O give 9:10-dihydroxy-1:2:9:10-tetramethyl-9:10-dihydroanthracene, m.p. 162—163°, the 9:10-(OMe)₂-derivative, m.p. 140—141.5°, of which could not be demethoxylated. F. R. S.

Action of acid clay on sterols. VIII. Action of acid clay on cholesterol. T. KAWASAKI and Z. YAMAMURA (J. Pharm. Soc. Japan, 1939, 59, 144—152; cf. A., 1939, II, 363).—Acid clay in boiling C₆H₆ converts cholesterol into a hydrocarbon (I), C₅₄H₈₈, m.p. 328.7° (decomp.; corr.), [α]_D -2.4° in CHCl₃, or, sometimes, isomeric hydrocarbons, m.p. 281.9° or 348.4°. (I) contains 2—3 ethylenic linkings (Bz₂O₂), with Br gives a substance, m.p. 140—200° (decomp.), is stable to H₂-PtO₂ in (iso-C₅H₁₁)₂O, Na-C₅H₁₁-OH, and CrO₃, and with boiling HNO₃ (*d* 1.4) gives a (?) C₆H₂Me(CO₂H)₃, m.p. ~230° (Me_x ester, m.p. 127°). (I) resembles the isomeric hydrocarbons, m.p. >300°, of Windaus (A., 1906, i, 174), and (new m.p. 301.3°) of Müller (A., 1933, 820). Distillation of the residues after separation of (I) at 0.5 mm. gives an oil, whence 3-cyclohexylcholestone is obtained by hydrogenation; the final residue when distilled at 0.05 mm. yields 3-phenylcholestone. R. S. C.

Aromatic hydrocarbons. XXIV. Hexacene, a green, simple hydrocarbon. E. CLAR (Ber., 1939, 72, [B], 1817—1821).—7:15-Dihydroxyhexacene-5:16:8:13-diquinone (I), red-brown needles



which become blue without melting at >300°, is obtained from 1:5-C₁₀H₆(OH)₂ and *o*-C₆H₄(CO)₂O either in presence of AlCl₃-NaCl at 210° or in C₂H₂Cl₄ containing AlCl₃ at 130°. It is best purified through the Na salt. (I), NaCl, ZnCl₂, and Zn dust at 210—280° afford 5:16- or 6:15-dihydrohexacene, m.p. 357—358° (vac.), which is dehydrogenated by Cu powder at 301—320°/vac. to hexacene, gradual decomp. >300°, which is very sparingly sol. in org. media; the green solutions are extremely sensitive to air and light and are immediately decolorised by maleic anhydride. H. W.

Anomalous halides. V. Anomalous halides of anthanthrene and attempted preparation of B (A., II.)

monohalides of peri-naphthindenone. K. BRASS and E. CLAR (Ber., 1939, 72, [B], 1882—1884).—Anthanthrene (I) and I in boiling C₆H₆ afford a triiodide, softens at 150° and melts slowly and with decomp. up to 250°. (I) and Br in C₆H₆ at 30° give a dark brown ppt. which rapidly passes into an orange-yellow product which contains (I) but no active Br. *peri*-Naphthindenone (II), like benzanthrone, gives dark-coloured compounds (III) with Br and I which contain active halogen and probably consist of 1 mol. of (II) with 1 atom of Br or I. (III) lose halogen when washed with C₆H₆. The formation of anomalous halides appears to demand a compact arrangement of the C₆H₆ nuclei; this, however, is not the only requirement. H. W.

Hydrogenation of aldehydes in presence of ammonia. C. F. WINANS (J. Amer. Chem. Soc., 1939, 61, 3566—3567).—In accordance with theory, hydrogenation (Raney Ni) in EtOH at 40—75° of a 2:1 mixture of RCHO (R = Ph, *o*-tolyl, *o*-C₆H₄Cl, or furfuryl) and NH₃ gives mainly NH(CH₂R)₂, of a 3:2 mixture gives equal amounts of NH₂·CH₂R and NH(CH₂R)₂, and of a 1:1 mixture gives mainly NH₂·CH₂R. Equally as expected, replacement of 3 mols. of RCHO and 2 mols. of NH₃ in the above mixtures by 1 mol. of preformed CHR(N:CHR)₂ gives similar results, confirming the reversibility of the synthesis of these compounds. The synthesis fails owing to aldol condensation if RCHO has a H on C_(α). R. S. C.

Sympathomimetics. Preparation of N-substituted β-phenylisopropylamines. A. NOVELLI (Anal. Asoc. Quím. Argentina, 1939, 27, 169—171).—Following a method previously recorded (A., 1939, II, 143) the following were prepared: β-methylamino-, m.p. 133—135°, β-ethylamino-, m.p. 145—146°, β-n-butylamino-, m.p. 168—169°, β-n-amylamino-, m.p. 186—187°, β-dimethylamino-, m.p. 156—158°, β-diethylamino-, m.p. 160—161°, and β-piperidino-, m.p. 206—208°, -α-phenylpropane hydrochlorides. F. R. G.

Addition of N-halogenoamides to olefines. M. S. KHARASCH and H. M. PRIESTLEY (J. Amer. Chem. Soc., 1939, 61, 3425—3432).—RSO₂·NR'Br adds to CHR''CH₂ to give RSO₂·NR'·CH₂·CHR''Br (A) (cf. "normal" addition to olefines), but RSO₂·NBr₂ reacts to give RSO₂·NH·CHR''·CH₂Br (B) (cf. "abnormal" addition) and C₂H₅R''Br. The structure of (A) is proved by removing HBr by quinoline or NaOEt-EtOH and then hydrogenating (Pd-BaSO₄) and hydrolysing (HCl; 150°), the final product, R''[CH₂]₂NHR', being also obtained from (A) in one step by Na-C₅H₁₁-OH. Hydrolysis of (B) gives ethyleneimine derivatives, the fission of which is investigated. Other N-Br-derivatives do not add to olefines. CHPh·CH₂ with PhSO₂·NMeBr gives α-bromo-β-benzenesulphonmethylamido-α-phenylethane (I), a syrup, and with *p*-C₆H₄Me·SO₂·NMeBr gives α-bromo-β-*p*-toluenesulphonmethylamido-α-phenylethane (II), m.p. 67° (Br readily removed by AgNO₃), converted by NaOAc into the α-OAc-compound, m.p. 94°, hydrolysed to the oily OH-derivative, which with Na-C₅H₁₁-OH gives β-hydroxy-β-phenylethylmethylamine, m.p. 78°. Boiling quinoline very rapidly or

NaOEt-EtOH more slowly converts (II) into β -*p*-toluenesulphonmethylamidostyrene, m.p. 106–107°; reduced by H_2 -Pd-BaSO₄ in MeOH to a syrup, which with conc. HCl at 150° gives Ph[CH₂]₂·NHMe (III) (hydrochloride, new m.p. 162°; mercurichloride, new m.p. 174°; oxalate, new m.p. 186°; carbamide derivative, new m.p. 143°), also obtained from (II) by Na-C₅H₁₁-OH. Fe-HCl reduces (I) to a syrup, which by hydrolysis gives (III). Similar reactions lead to α -*bromo*- β -benzene-, a syrup, and α -*bromo*- β -*p*-toluenesulphonbenzylamido- α -phenylethane, m.p. 99°, β -*p*-toluenesulphonbenzylamidostyrene, m.p. 122°, β -*p*-toluenesulphonbenzylamidoethylbenzene, m.p. 105° (and thence Ph[CH₂]₂·NH·CH₂Ph), benzene-, m.p. 95°, and *p*-toluenesulphonmethyl- β -bromoisobutylamide (from CMe₂·CH₂ and RSO₂·NMeBr), m.p. 93°, *toluene*- ω -sulphonmethyl- β -bromoisobutylamide, m.p. 123°, α - or γ -benzenesulphonmethylamido- β -methylpropene, an oil (by reduction and hydrolysis gives NHMeBu⁸), α - or γ -toluene- ω -sulphonmethylamido- β -methylpropene, m.p. 60°, *toluene*- ω -sulphonmethylisobutylamide, m.p. 83°, α -chloro- α -*bromo*- β -benzene-, m.p. 90°, and β -*p*-toluene-sulphonmethylamidodiphenylmethane (from CH₂·CHCl), m.p. 90°, β -*p*-toluenesulphonmethylamidovinyl chloride, m.p. 91°, β -*bromo*- α -*p*-toluenesulphonmethylamidopropane, m.p. 92°, α - and γ -*p*-toluenesulphonmethylamidopropene, m.p. 54–56°, and an oil (or vice versa), and *p*-toluenesulphonmethyl-*n*-propylamide, m.p. 40° (hydrolysed to NHMePr⁸). *p*-C₆H₄Me·SO₂·NBr₂ and CHPh·CH₂ in warm CHCl₃ give β -*bromo*- α -phenyl- α -*p*-toluenesulphonamidoethane (IV), m.p. 167° (Br stable to AgNO₃ and NaOAc-AcOH). Similarly are obtained β -*bromo*- α -*p*-toluenesulphonamido- α -*p*-anisyl-, m.p. 167°, and α -3:4-methylenedioxyphenyl-propane, m.p. 153°. Hot NaOH-EtOH-H₂O converts (IV) into *N*-*p*-toluenesulphonylstyreneimine (V), m.p. 95°, stable to KMnO₄ (the olefines named above reduce KMnO₄), which with cold, aq. HHal gives α -chloro-, m.p. 95°, α -*bromo*- (VI), m.p. 111°, and α -iodo- β -*p*-toluenesulphonamidoethylbenzene, m.p. 137°. The *N*-Br-derivative of (VI) with CHPh·CH₂ gives α -*bromo*- β -*p*-toluenesulphon- β' -*bromo*- α' -phenylethylamidodiphenylbenzene, m.p. 158°. Hydrogenation (Pd-BaSO₄; MeOH) of (V) gives *p*-C₆H₄Me·SO₂·NH·[CH₂]₂·Ph (VII), m.p. 67° (lit. 65–66°), hydrolysed to Ph[CH₂]₂·NH₂, which is obtained directly from (V) by Na-C₅H₁₁-OH. The *N*-Br-derivative of (VII) with CHPh·CH₂ gives α -*bromo*- β -*p*-toluenesulphon- β' -phenylethylamidodiphenylbenzene, m.p. 97°. In hot H₂O, (V) gives *p*-toluenesulphon- β -hydroxy- β -phenylethylamide, m.p. 113°, hydrolysed to OH·CHPh·CH₂·NH₂ (VIII) (picrate, m.p. 158°) by Na-C₅H₁₁-OH. With hot RCO₂H, (V) gives β -*p*-toluenesulphonamido- α -trichloroacetoxy-, m.p. 125° [hydrolysed to (VIII)], α -crotonoxy-, m.p. 85° [hydrolysed to (VIII)], and α -acetoxy-ethylbenzene, m.p. 105° [obtained also from (VI) by NaOAc-AcOH]. Cold H₂SO₄-EtOH or a little CCl₃·CO₂H in boiling EtOH converts (V) into β -*p*-toluenesulphonamido- α -ethoxy-ethylbenzene, m.p. 106°. R. S. C.

Action of nitrosyl chloride on monobromomalonamides. M. P. SHAH and V. B. THOSAR (J. Indian Chem. Soc., 1939, 16, 556).—CHBr(CO·NH·C₆H₄Me-*p*)₂ or CHBr(CO·NH·CH₂Ph)₂ in C₆H₆ with NOCl at 0°

yields respectively *chlorobromomalon-p-toluidide*, m.p. 135°, or *-benzylamide*, m.p. 153°. F. R. G.

Oxidation of heteronuclear-substituted polybromodiphenyls. F. H. CASE (J. Amer. Chem. Soc., 1939, 61, 3487–3490).—Oxidation of polybromodiphenyls by CrO₃ in 75% AcOH and isolation of the bromobenzoic acids formed (given in brackets below) indicates the following order of decreasing radical stability to oxidation: 4-bromo- > 3:5-dibromo- > 2:5-dibromo-, 3-bromo- > 2-bromo- > 2:4:6-tribromo-phenyl. 4:3-NH₂·C₆H₃Br·C₆H₄Br-*o* gives (diazo-reaction) 2:3'-*dibromodiphenyl*, b.p. 165–168°/3 mm. [gives *m*-C₆H₄Br·CO₂H (I)]. *o*-NH₂·C₆H₄·C₆H₄Br-*m* yields by the usual reactions successively 3:5:3'-*tribromo-2-aminodiphenyl*, m.p. 111–112° (*Ac* derivative, m.p. 185–186°), and 3:3':5'-*tribromodiphenyl*; m.p. 112–113° [gives 3:5:1-C₆H₃Br₂·CO₂H (II)]. 4:3:5-NH₂·C₆H₂Br₂·C₆H₄Br-*p* yields 3:5:4'-*tribromodiphenyl*, m.p. 102–103° (cf. Bellavita, A., 1938, II, 9) [gives *p*-C₆H₄Br·CO₂H (III)]. *m*-NHAc·C₆H₄·C₆H₄Br-*p* gives successively 2:4'-*dibromo-5-acetamido*-, m.p. 163–164°, 2:4'-*dibromo-5-amino*-, m.p. 91–92° (yields *o*-C₆H₄Br·C₆H₄Br-*p*), and 2:5:4'-*tribromo-diphenyl*, m.p. 77–78° (cf. *idem*, A., 1935, 1488) [gives (III) and 2:5:1-C₆H₃Br₂·CO₂H (IV)]. *o*-NH₂·C₆H₄·C₆H₄Br-*m* gives 3-*bromo-2'-acetamidodiphenyl*, m.p. 93–94°, and thence 3:3'-*dibromo-6-acetamido*-, m.p. 145–146°, the derived amine [gives (*m*-C₆H₄Br)₂], and 2:5:3'-*tribromo-diphenyl*, b.p. 213–216°/6 mm. [gives (I) and (IV)]. *o*-C₆H₄Br·C₆H₄·NHAc-*m* gives 2:2'-*dibromo-5-acetamido*-, m.p. 142°, and thence 2:5:2'-*tribromo-diphenyl*, m.p. 77–78° [gives (IV)]. *p*-C₆H₄Br·C₆H₄·NHAc-*m* gives 2:4:6:4'-*tetrabromo-3-acetamido*-, m.p. 260–261°, 2:4:6:4'-*tetrabromo-3-amino*-, m.p. 93–94° (lit. 104°), and 2:4:6:4'-*tetrabromo-diphenyl*, m.p. 105–106° [gives (III)]. Oxidation of 1:2:4:6-C₆H₂PhBr₃ (prep. from PhI, 2:4:6:1-C₆H₂Br₃I, and Cu powder at 180° and later 200°), m.p. 65–66°, gives also some (III), presumably owing to formation of free Br during the reaction. 3-Nitrobenzidine gives only a *monourethane*, m.p. 167–168°, which affords 5-*bromo-3-nitrobenzidine-urethane*, m.p. 167–168°, and thence the free base, and 1:5:3-C₆H₃PhBr·NO₂, m.p. 71–72°. 5-*Bromo-3-aminodiphenyl*, m.p. 89–90° (*Ac* derivative, m.p. 142–143°), is also described. R. S. C.

Sulphanilamide derivatives. II. Arylidene derivatives of N⁴-substituted sulphanilamides. H. G. KOLLOFF and J. H. HUNTER (J. Amer. Chem. Soc., 1940, 62, 158–160; cf. A., 1938, II, 228).—In general, transformation of *p*-NH₂·C₆H₄·SO₂·NHR (*A*) into *p*-R'·CH·N·C₆H₄·SO₂·NHR decreases the anti-streptococcal and -pneumococcal activity and the toxicity. The following are prepared from (*A*) and RCHO (no solvent); owing to instability and ease of hydrolysis, care is needed during recrystallisation. *N*⁴-Benzylidene-, m.p. 176°, *-p*-anisylidene-, m.p. 192–193°, and *-p*-dimethylaminobenzylidene-sulphonamide, m.p. 226–227°. *Benzylidene*-, m.p. 175–175.5°, *-p*-anisylidene-, m.p. 166°, and *-p*-dimethylaminobenzylidene-sulphanilanilide, m.p. 231°. *Benzylidene*-, m.p. 192°, *-p*-anisylidene-, m.p. 213.5°, and

p-dimethylaminobenzylidene-sulphanil-*p*-nitroanilide, m.p. 231°. 2-Benzylidene-, m.p. 245—246°, 2-*p*-anisylidene-, m.p. 212—212.5°, and 2-*p*-dimethylaminobenzylidene-sulphanilamidopyridine, m.p. 238.2—240°.

R. S. C.

sec. Amines from nitro-compounds. W. S. EMERSON and H. W. MOHRMAN (J. Amer. Chem. Soc., 1940, **62**, 69—70).—Hydrogenation at 40 lb. of ArNO_2 and an aliphatic or aromatic aldehyde in EtOH in presence of Raney Ni and NaOAc gives 31—96% of NHArR , in which (a) $\text{Ar} = \text{Ph}$, $\text{R} = \text{Me}$, Et , Bu^a , $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_7\text{H}_{15}$, or CH_2Ph , (b) $\text{Ar} = p\text{-OMe-C}_6\text{H}_4$, $\alpha\text{-C}_{10}\text{H}_7$, or *p*-tolyl, $\text{R} = \text{Bu}^a$, (c) $\text{Ar} = \alpha\text{-C}_{10}\text{H}_7$, $\text{R} = n\text{-C}_5\text{H}_{11}$, and (d) $\text{Ar} = p\text{-tolyl}$, $\text{R} = n\text{-C}_7\text{H}_{15}$. Except when $\text{Ar} = p\text{-tolyl}$, no *tert.* amines are formed. *p*-Bromobenzenesulphon-N-butyl-*p*-aniside, m.p. 72—73°, *p*-chlorobenz-N-n-butyl-, m.p. 242—243°, and *p*-bromobenz-N-n-amyl- α -naphthylamide, m.p. 226—227°, *p*-bromobenzenesulphon-N-n-heptyl-*p*-toluidide, m.p. 52—52.5°, *NN*-di-*n*-butyl- (53% formed), new b.p. 295—296° (*picrate*, m.p. 186—187°), and *NN*-di-*n*-heptyl-*p*-toluidine (34% formed), b.p. 175—200°/2.5 mm. (*hydrochloride*, m.p. 136°), are incidentally described.

R. S. C.

Additive compounds of dicyclohexylamine [etc.]. C. F. WINANS (J. Amer. Chem. Soc., 1939, **61**, 3591—3592).—1:1 additive compounds (m.p. below) are formed when dicyclohexylamine is mixed in, e.g., petroleum ether with cyclohexanol (I), m.p. 47—48°, 4-*tert*-butyl-, m.p. 75—76°, and 2-methylcyclohexanol, m.p. 59—60°, cyclohexane-1:2-, m.p. 64—66°, -1:3- (II), m.p. 64—66°, and -1:4-diol, m.p. 90—91°. 2-cyclohexylcyclohexanol, m.p. 43—45°, $\text{Ph}[\text{CH}_2]_2\text{OH}$, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and $\text{CH}_2\text{Ph}\cdot\text{OH}$, m.p. < room temp. Similar compounds, m.p. < room temp., are obtained from $\text{NH}(\text{CH}_2\text{Ph})_2$ or cyclohexylamine with (I) and from piperidine and (II).

R. S. C.

Arylamino-naphthalenesulphonic acids.—See B., 1940, 117.

Condensation products of *m*-dialkylaminobenzaldehydes with compounds containing reactive methylene groups. W. COCKER and D. G. TURNER (J.C.S., 1940, 57—59).—1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$, *m*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and piperidine (I) at 100° (bath) give 2:4-dinitro-3'-dimethylaminostilbene, m.p. 205°, and similar condensations afford 2:4-dinitro-3'-diethyl-, m.p. 153°, -dipropyl-, m.p. 132°, and -dibenzyl-aminostilbene, m.p. 163°. With $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$, the following are obtained: 3-dimethyl-, m.p. 162.5°, 3-diethyl-, m.p. 136°, 3-dipropyl-, m.p. 108°, and 3-diallyl-amino- α -*p*-nitrophenylcinnamionitrile, m.p. 82°. $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ gives 3-dimethylamino- α -*p*-nitrophenylcinnamic acid, m.p. 215.5°, which with (I) at 140—145° affords 4-nitro-3'-dimethylaminostilbene, m.p. 145—145.5°; similarly prepared are 3-diethyl-, m.p. 173°, and 3-dipropyl-amino- α -*p*-nitrophenylcinnamic acid, m.p. 180.5°, and 4-nitro-3'-diethyl-, m.p. 97°, and -dipropyl-aminostilbene, m.p. 79°. Using (I) as condensing agent the following are obtained: 1-phenyl-4-*m*-dimethylaminobenzylidene-5-pyrazolone, m.p. 117°, 2-m-dimethyl-, m.p. 237°, 2-*m*-diethyl-, m.p. 208°, and 2-*m*-dipropyl-aminostyrylpyridine methiodide, m.p.

192°; 2-*m*-dimethylaminostyrylquinoline methiodide, m.p. 261°; 2-*m*-dimethylaminostyrylthiazole methiodide, m.p. 218°; and 2-*m*-dimethyl-, m.p. 205°, and 1-*m*-diethyl-aminostyrylbenzthiazole methiodide, m.p. 188°. Many of these substances give dyes on acetate silk but their light-fastness is poor.

F. R. S.

Conjugation of amino-acids with carbimides of the anthracene and 1:2-benzanthracene series. L. F. FIESER and H. J. CREECH (J. Amer. Chem. Soc., 1939, **61**, 3502—3506).—2-Aminoanthracene, m.p. 243.5—244.5° [245—245.5° (vac.); lit. 236—237°, 238° (uncorr.)], and COCl_2 in boiling $\text{PhMe}\cdot\text{C}_6\text{H}_6$ give 2-carbimidoanthracene, m.p. 207.5—208°, and thence *Me*, m.p. 231—231.5°, and *Et* 2-anthrilylcarbamate, m.p. 216—216.5°, *N*-2-anthrilyl-*N'*- β -hydroxyethyl-, m.p. ~350° (darkens at 310°), *N*-2-anthrilyl-, m.p. >360°, and *s*-di-2-anthrilyl-carbamide, m.p. >340°, and (by condensing with the NH_2 -acid in aq. dioxan at p_H 8.5 at 40°) *N*-2-anthrilyl-*N'*-carboxymethyl-, darkens at 250°, m.p. ~310° (decomp.; vac.), and -*N'*- ϵ -carboxy-*n*-amyl-carbamide, darkens at 260°, m.p. 285—286° (vac.). 1:2-Benzanthracene (modified prep.) gives 25—45% of the 10- NO_2 - and thence 77% of the 10- NH_2 -compound, m.p. 175.5—176° [176—176.5° (vac.)], which yields the 10-carbimido-derivative, m.p. 144—144.5° [in $\text{C}_6\text{H}_5\text{N}$ at room temp. gives a polymeride, m.p. 305—307° (vac.)], and thence *Me*, m.p. 227—227.5°, and *Et* 1:2-benzanthrilyl-10-carbamate, m.p. 204—204.5°, *N*-1:2-benzanthrilyl-10-*N'*- β -hydroxyethyl-, darkens at 240°, m.p. 247—248° (vac.), and *s*-di-1:2-dibenzanthrilyl-10-carbamide, amorphous, m.p. >330°, 1:2-benzanthrilyl-10-carbamide, m.p. 334—336° (decomp.; vac.), *N*-1:2-benzanthrilyl-10-*N'*-carboxymethyl-, amorphous, darkens at 230—240°, m.p. ~270—275° (decomp.) (*Et* ester, m.p. 245—245.5°), and -*N'*- ϵ -carboxy-*n*-amyl-carbamide, darkens at 200°, m.p. 265—267°. Similarly are obtained 1:2:5:6-dibenzanthrilyl-9-carbamide, m.p. 360—363° (decomp.; vac.), *N*-1:2:5:6-dibenzanthrilyl-9-*N'*-carboxymethyl-, darkens at 270°, m.p. ~300° (decomp.), and -*N'*- ϵ -carboxy-*n*-amyl-carbamide, yellow at ~250°, m.p. ~305°, 3-carbimido-1:2-benzanthracene, m.p. 163—163.5° (polymerises in $\text{C}_6\text{H}_5\text{N}$ at 25°), *Me* m.p. 203.5—204°, and *Et* 1:2-benzanthrilyl-3-carbamate, m.p. 211.5—212°, *N*-1:2-benzanthrilyl-3-*N'*- β -hydroxyethylcarbamide, m.p. 343—345° (vac.), 1:2-benzanthrilyl-3-carbamide, m.p. >350°, *s*-di-1:2-benzanthrilyl-3-carbamide, m.p. >350°, *N*-1:2-benzanthrilyl-3-*N'*-carboxymethyl-, m.p. ~310° (decomp.; vac.), and -*N'*- ϵ -carboxy-*n*-amyl-carbamide, darkens at 230°, m.p. 295—297°. 3-Amino-1:2-benzanthracene has m.p. 211—212° [213.5—214° (vac.)]. *s*-Di-9-anthranylcaramide has m.p. >360°. M.p. <275° are corr.

R. S. C.

Identification of organic acids by the use of *p*-chlorobenzyl- ψ -thiuronium chloride. B. T. DEWEY and R. B. SPERRY (J. Amer. Chem. Soc., 1939, **61**, 3251—3252).—*p*-Chlorobenzyl- ψ -thiuronium chloride [prep. from $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$ and $\text{CS}(\text{NH}_2)_2$ in boiling EtOH], m.p. 197°, and RCO_2Na (or K) (neutral) in aq. EtOH give the acetate, m.p. 140°, butyrate, m.p. 139°, hexoate, m.p. 143°, formate, m.p. 148°, mono-, m.p. 158°, and tri-chloroacetate, m.p. 148°, oleate, m.p. 131°, oxalate, m.p. 194°, palmitate, m.p. 146°, pro-

pionate, m.p. 143°, succinate, m.p. 167°, valerate, m.p. 142°, benzenesulphonate, m.p. 184°, benzoate, m.p. 155°, o-, m.p. 165°, m-, m.p. 161°, and p-bromo-, m.p. 172°, o-, m.p. 159°, m-, m.p. 157°, and p-chloro-, m.p. 173°, o-, m.p. 162°, m-, m.p. 154°, and p-iodo-benzoate, m.p. 177°, cinnamate, m.p. 167°, phthalate, m.p. 166°, salicylate, m.p. 162°, sulphosalicylate, m.p. 181°, o-, m.p. 150°, m-, m.p. 151°, and p-toluate, m.p. 161°, and p-toluenesulphonate, m.p. 193°, best recrystallised from dioxan.

R. S. C.

Alkamine esters of disubstituted methylcarbamic acids. J. J. DONLEAVY and J. ENGLISH, jun. (J. Amer. Chem. Soc., 1940, 62, 218—219).— CHPh_2NCO (prepared from CHPh_2Br and AgNCO in boiling Et_2O or, *in situ*, from CHPh_2COCl and NaN_3 in COMe_2 at 0°), b.p. 148°/4 mm., with the appropriate NH_2 -alcohol in boiling Et_2O gives β -diethylaminoethyl, m.p. 179°, γ -diethylamino-n-propyl, m.p. 183°, β -dibutylaminoethyl, m.p. 136°, and β -piperidinoethyl, m.p. 119°, diphenylmethylcarbamate hydrochloride. CHPhMeBr and AgNCO give similarly CHPhMeNCO , b.p. 96°/18 mm., and thence β -diethylaminoethyl, b.p. 178°/5 mm., and γ -diethylamino-n-propyl α -phenylethylcarbamate, b.p. 164°/3 mm. Pr^nBr yields similarly β -diethylaminoethyl isopropylcarbamate, b.p. 123—125°/5 mm. (hydrochloride, m.p. 114°). The carbamates are powerful, but irritating, local anaesthetics.

R. S. C.

Feeding experiments on white rats with 4'-amino-2 : 3'-dimethylazoxybenzene. N. NAGAO (Proc. Imp. Acad. Tokyo, 1939, 15, 321—325).—4'-Acetamido-2 : 3'-dimethylazoxybenzene, m.p. 149—150° (from the azo-compound and H_2O_2 in aq. AcOH), is hydrolysed (EtOH -conc. HCl) to 4'-amino-2 : 3'-dimethylazoxybenzene (I), m.p. 92—93°. When fed to white rats over periods of 200—250 days, (I) causes hypertrophy of the liver, proliferation of the epithelia of the bile duct, and formation of thromboses in the veins of the liver.

J. D. R.

Preparation of m-halogenophenols. H. H. HODGSON (J. Amer. Chem. Soc., 1940, 62, 230).—Concerning priority (A., 1923, i, 1005).

R. S. C.

Rearrangement of the triphenylmethyl ethers of o-cresol and brominated o-cresols. H. A. IDDLIS, W. H. MILLER, and W. H. POWERS (J. Amer. Chem. Soc., 1940, 62, 71—73).—Condensation of o-cresol and CPh_3OH by H_2SO_4 is shown to yield 5 : 1 : 2- $\text{CPh}_3\text{C}_6\text{H}_3\text{MeOH}$ (I) (cf. A., 1940, II, 12). 1 : 3 : 2- $\text{C}_6\text{H}_3\text{MeBrOH}$ (II), CPh_3OH , and H_2SO_4 in AcOH give 55% of 3-bromo-5-triphenylmethyl-o-cresol (III), m.p. 149—151°, which is also obtained from (I) by Br and a little Fe in CCl_4 and is methylated ($\text{Me}_2\text{SO}_4\text{NaOH}$) to 5 : 1 : 3 : 2- $\text{CPh}_3\text{C}_6\text{H}_2\text{MeBrOMe}$, also obtained by brominating the condensation product from o- $\text{C}_6\text{H}_3\text{MeOMe}$ and CPh_3OH (cf. *loc. cit.*). 1 : 5 : 2- $\text{C}_6\text{H}_3\text{MeBrOH}$ (IV), CPh_3OH , and $\text{H}_2\text{SO}_4\text{AcOH}$ give 6.75% of 5-bromo-3-triphenylmethyl-o-cresol, m.p. 208—209°, but 1 : 3 : 5 : 2- $\text{C}_6\text{H}_3\text{MeBr}_2\text{OH}$ (V) (prep. from o-cresol by Br-CCl_4), m.p. 56.5—57.5°, gives no analogous product. Attempts to prepare the ether from (II) and CPh_3Cl give only (III), whereas (V) does not react and (IV) gives 48.7% of

5-bromo-o-tolyl CPh_3 ether, m.p. 113.5—114°, stable to HCl or ZnCl_2 in $\text{AcOH-H}_2\text{SO}_4$.

R. S. C.

Chloro- and bromo-hydroxyalkyldiphenyls.—See B., 1940, 117.

Isomerisation during distillation with zinc dust. A. LÜTTRINGHAUS and G. VON SÄÄF (Ber., 1939, 72, [B], 2026—2028).—Distillation of 2 : 6 : 1- $\text{C}_6\text{H}_3\text{Ph}_2\text{OH}$ with Zn dust yields p- $\text{C}_6\text{H}_4\text{Ph}_2$, m.p. 207°, further identified by conversion into the 4' : 4''-(NO_2)₂-derivative, m.p. 273°. With Zn dust in $\text{ZnCl}_2\text{-NaCl}$ at 280—340° there is scarcely any action apart from formation of small amounts of resin.

H. W.

Cyclialkylation of aromatic compounds by the Friedel-Crafts reaction. H. A. BRUSON and J. W. KROEGER (J. Amer. Chem. Soc., 1940, 62, 36—44).—The term "cyclialkylation" is applied to a reaction whereby an alkylene group is attached at two points to an aromatic nucleus with formation of a new ring. Numerous examples are provided. AlCl_3 , H_2SO_4 , or BF_3 is usually needed as catalyst. The products sometimes vary according to the catalyst or conditions. Structures of products are assigned by analogy without rigid proof. $\beta\epsilon$ -Dimethyl- Δ^7 -hexinene- $\beta\epsilon$ -diol, m.p. 94—95°, obtained in 98% yield by adding COMe_2 (5.25) to CaC_2 (1.75) and KOH (3.5 mols.) in C_6H_6 at 21—24°, is hydrogenated (Raney Ni) in H_2O or EtOH at 60—85°/7 atm. to $\beta\epsilon$ -dimethyl-n-hexane- $\beta\epsilon$ -diol (I) (95—99%), m.p. (+6 H_2O) 38° or (anhyd.) 88—89°, which (a) with saturated, aq. HCl at room temp. gives the $\beta\epsilon$ -dichloride (II), m.p. 63—64°, or (b), when distilled with 3% of $\text{NH}_2\text{Ph.HBr}$, gives 2 : 2 : 5 : 5-tetramethyltetrahydrofuran (III), b.p. 112—114°/768 mm., and a little $\beta\epsilon$ -dimethyl- Δ^{88} -hexadiene. $\beta\epsilon$ -Dimethyl- Δ^{88} -hexadiene (IV), b.p. 114.5°/763 mm., is obtained from 2 mols. of $\text{CH}_2\text{CMe-CH}_2\text{Cl}$ and 1 Mg. PhOH , (II), and a little AlCl_3 in light petroleum (b.p. 90—100°), first at room temp. and then at 100°, give 80% of 5 : 5 : 8 : 8-tetramethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthol (V), m.p. 145—145.2°, and a little 2 : 2-dimethyl-4-isopropyl-6 : 7-octadec-tetramethylmethylene-3 : 4-dihydrochroman (VI), m.p. 240—241°. PhOH with (a) (I) and AlCl_3 (large amount) in petroleum naphtha at 85—90°, (b) (III) and AlCl_3 (large amount) in petroleum ether, first at room temp. and then at 100°, or (c) (IV) and a little AlCl_3 in petroleum ether, first at 0°, then at 25°, and finally at 50°, also give (V). Oxidation of (V) by KMnO_4 to $(\text{CH}_2\text{CMe}_2\text{CO}_2\text{H})_2$, m.p. 190—193°, proves absence of rearrangement. 5 : 5 : 8 : 8-Tetramethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthyl-oxyacetic acid, m.p. 164—165°, and the *Et* ether, b.p. 132°/5 mm. (NO_2 -derivative, m.p. 106—108°), of (V) are obtained from (V) by the usual methods and by condensing (AlCl_3) (II) with $\text{OPh-CH}_2\text{CO}_2\text{H}$ in $(\text{CH}_2\text{Cl})_2$ at room temp. or PhOEt , respectively. In presence of HCl , aq. CH_2O and (V) give 1 : 1'-methyl-enedi-5 : 5 : 8 : 8-tetramethyl-5 : 6 : 7 : 8-tetrahydro-2-naphthol, m.p. 232°. The appropriate phenol or ether with (II) and AlCl_3 (details as for PhOH) gives 3 : 5 : 5 : 8 : 8-, m.p. 125.5—126°, and 4 : 5 : 5 : 8 : 8-pentamethyl-, m.p. 134—135°, 1 : 3 : 5 : 5 : 8 : 8-hexamethyl- (VII), m.p. 164.5°, unstable in air, 3-phenyl-5 : 5 : 8 : 8-tetramethyl-, m.p. 98°, 3-cyclohexyl-5 : 5 : 8 : 8-tetramethyl-, m.p. 109—110°, 3-chloro-5 : 5 : 8 : 8-tetra-

methyl-, m.p. 103.5–104°, and 4- β - β' -chloroethoxyethoxy-5:5:8:8-tetramethyl-, isomerides, m.p. 107–108° and 71–75°, -5:6:7:8-tetrahydro-2-naphthol and 6:7-dihydroxy-1:1:4:4-tetramethyl-1:2:3:4-tetrahydronaphthalene, m.p. 182–183°. However, diphenylene oxide, (II), and a little AlCl_3 give 2:3- $\alpha\alpha\delta\delta$ -tetramethyltetramethylene-, b.p. (impure) 170–240°/4 mm., and 2:3-6:7-di- $\alpha\alpha\delta\delta$ -tetramethyltetramethylene-diphenylene oxide, m.p. 201–202°. *p*-Cresol, (II), and a little AlCl_3 (as for PhOH) give (?) 4-methyl-1:2-diisopropyl-1:2-dihydrocoumarone (VIII), b.p. 107–108°/1 mm. (minty odour), 2:2:6 (or 4:4:6)-trimethyl-4(or 2)-isopropyl-3:4-dihydrochroman, m.p. 100–101°, and a small amount of a dicyclicalkylated compound (IX), $\text{C}_{23}\text{H}_{26}\text{O}$, m.p. 193–195°. 77% H_2SO_4 , successively at 10°, 35°, room temp., and 85–95°, causes condensation of PhOH and (I) to 5-hydroxy-1:1-dimethyl-3-isopropylhydrindene (X), m.p. 97–98° (oxyacetic acid, m.p. 112–113°; unchanged by AlCl_3 or CH_2O ; with KMnO_4 gives no identifiable acid), probably by rearrangement of the intermediate radical, $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot[\text{CH}_2]_2\cdot\text{CMe}_2\cdot$ to $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHPr}^{\beta}$; similarly, (I) and 2:6:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ with AlCl_3 or 77% H_2SO_4 give (VII) or a compound, $\text{C}_{16}\text{H}_{24}\text{O}$, b.p. 156°/6 mm., respectively. With BF_3 at 90° in place of AlCl_3 , *p*-cresol and (IV) give (IX) and a little (VIII), but with BF_3 at 0° PhOH and (IV) give (V), (VI), and (X). $(\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2)_2$ with PhOH or $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ gives (AlCl_3) mainly $(\text{CPh}_2\cdot\text{CH})_2$, but with *o*-cresol and AlCl_3 (large amount) in boiling petroleum ether (b.p. 30–60°) gives much 4:4:8:8-tetraphenyl-3-methyl-5:6:7:8-tetrahydro-2-naphthol, m.p. 330–332°, with a little $(\text{CPh}_2\cdot\text{CH})_2$. 1:4-Dichlorocyclohexane, PhOH, and a little AlCl_3 [as with (II)] give (?) 5:8-endoethylene-5:6:7:8-tetrahydro-2-naphthol, m.p. 124–127°. Neither AlCl_3 nor BF_3 causes cyclization of thiophenols by (II) or (IV), the sole products being $(\text{CH}_2\cdot\text{CMe}_2\cdot\text{SAr})_2$. Thus are obtained $\beta\epsilon$ -di-phenyl-, m.p. 79–80°, -*o*-, m.p. 75–76°, -*m*-, m.p. 105–106°, and -*p*-tolyl-, m.p. 128–129°, -thiol- $\beta\epsilon$ -dimethyl-n-hexane. In presence of much AlCl_3 , C_6H_6 and (II), first at $\geq 30^\circ$ and then boiling, give 61% of 1:1:4:4-tetramethyl-1:2:3:4-tetrahydronaphthalene, b.p. 82–84°/3 mm., 248°/760 mm., but in presence of only a little AlCl_3 give mainly 1:1:4:4:5:5:8:8-octamethyl-1:2:3:4:5:6:7:8-octahydroanthracene, m.p. 221–222° (NO_2 -derivative, m.p. 259–261°). PhMe, $o\text{-C}_6\text{H}_4\text{MeCl}$, 1:2:3:4-tetrahydronaphthalene, and hydrindene undergo only monocyclization, yielding 1:1:4:4:6-pentamethyl-, b.p. 95°/4 mm., and 7-chloro-1:1:4:4:6-pentamethyl-1:2:3:4-tetrahydronaphthalene, m.p. 104–105°, 1:1:4:4-tetramethyl-1:2:3:4:5:6:7:8-octahydroanthracene, m.p. 90–91°, and 5:5:8:8-tetramethyl-5:6:7:8-tetrahydro- β -naphthindane, m.p. 93–94°, respectively, but C_{10}H_8 gives 1:1:4:4:7:7:10:10-octamethyl-1:2:3:4:7:8:9:10-octahydronaphthacene, m.p. 319–320°. Thiophen, (II), and SnCl_4 in petroleum ether, first at room temp. and then boiling, give 3:3:6:6-tetramethyl-3:4:5:6-tetrahydrothionaphthen, b.p. 94°/6 mm. R. S. C.

Propionylation of naphthols in pyridine. A. LÉMAN (Compt. rend., 1940, 210, 78–80; cf. A.,

1938, II, 274).— α - and β - $\text{C}_{10}\text{H}_7\text{-OH}$ (0.01 mol.) and 1:7- $\text{C}_{10}\text{H}_6(\text{OH})_2$ (0.005 mol.) are propionylated completely at 35° in 15 min. with a mixture (5 c.c.) of equal vols. of $\text{C}_5\text{H}_5\text{N}$ and $(\text{EtCO})_2\text{O}$. After hydrolysis of excess of $(\text{EtCO})_2\text{O}$ with H_2O (50 c.c.) at 100°/15 min., the EtCO_2H is titrated with *N*-KOH. Even in presence of H_2O (50 c.c.), the $\text{C}_{10}\text{H}_7\text{-OH}$ react nearly quantitatively. 1:7:3- $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{SO}_3\text{H}$ partly reacts (18.2%) at 100°/1 hr. J. L. D.

Mills-Nixon effect. W. C. LOTHROP (J. Amer. Chem. Soc., 1940, 62, 132–133).—The Mills-Nixon effect (fixation of linkings) is only qual, in the case of hydrindene. Coupling of 5-hydroxy-6-methylhydrindene (I) with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{HSO}_4$ is decreased by increasing amounts of NaOH . Quant. experiments at p_H 7.5 and 11.3 and in 10% NaOH show that (I), 5-hydroxy-4:7-dimethylhydrindene, and 6-hydroxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene resemble *m*-4-xylenol rather than β - $\text{C}_{10}\text{H}_7\text{-OH}$. 5-Allyloxy-6-methylhydrindene, b.p. 95–97°/3 mm., in NPhMe_2 at 245° gives 86% of 5-hydroxy-6-methyl-4-allylhydrindene, m.p. 43–45°. 5-Allyloxy-4:7-dimethylhydrindene, b.p. 107–108°/2 mm., gives similarly at 280° 75% of 5-hydroxy-4:7-dimethyl-6-allylhydrindene, m.p. 66–67°. R. S. C.

Oestrogenic substances produced during demethylation of anethole. N. R. CAMPBELL, E. C. DODDS, and W. LAWSON (Proc. Roy. Soc., 1940, B, 128, 253–262; cf. A., 1939, II, 312).—Partly a more detailed account of work previously reviewed (A., 1939, III, 264). Demethylation (EtOH-KOH at 200°; whereby H_2 is produced) of anethole (I), remethylation (Me_2SO_4) of the product, removal of re-formed (I) by steam-distillation, and subsequent fractionation give fractions, b.p. up to 150°/0.15–0.2 mm. (A) and 160–170°/0.15–0.2 mm. (B). Demethylation (EtOH-KOH) of (A) affords phenols containing $p\text{-C}_6\text{H}_4\text{Pr}^a\cdot\text{OH}$ (3:5-dinitrobenzoate, m.p. 118°). Oxidation (KMnO_4 , COMe_2) of (B) gives anisic acid and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{COMe}$ (II) which arise from the $\alpha\gamma$ -dianisyl- β -methyl- Δ^a -pentene present; $\gamma\delta$ -dianisylhexane (III), m.p. 144° [converted by EtOH-KOH at 200° into $\gamma\delta$ -di-*p*-hydroxyphenylhexane (IV), m.p. 184–185°], and crude (V) (below) [whence (VI)] are isolated from the material resistant to oxidation. The yield of (IV) is 0.01–0.02% of the (I) initially used. *iso*Anethole (Goodall *et al.*, A., 1931, 85) is demethylated (EtOH-KOH at 200°) to $\alpha\gamma$ -di-*p*-hydroxyphenyl- β -methyl- Δ^a -pentene, b.p. 184–185°/0.15 mm. (purified through the diacetate, b.p. 282–289°/25 mm.), and reduced (H_2 , Pd, COMe_2) to $\alpha\gamma$ -dianisyl- β -methylpentane (V), b.p. 167°/0.08–0.09 mm., which is demethylated (EtOH-KOH at 170°) to $\alpha\gamma$ -di-*p*-hydroxyphenyl- β -methylpentane (VI), m.p. 128°. $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COMe}$ and $\text{Al} + \text{HgCl}_2$ in C_6H_6 (first in absence and then in presence of H_2O) give $\alpha\delta$ -dianisyl- $\beta\gamma$ -dimethylbutane- $\beta\gamma$ -diol, m.p. 135°, dehydrated ($\text{Ac}_2\text{O-AcCl}$) to $\alpha\delta$ -dianisyl- $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 163–164°, which is reduced (H_2 , Pd, COMe_2) to the -butane, m.p. 82–83°; this is demethylated [AcOH-HI (*d* 1.94) at 140°] to $\alpha\delta$ -di-*p*-hydroxyphenyl- $\beta\gamma$ -dimethylbutane, m.p. 151–152°. α -Anisylpropyl *p*-methoxystyryl ketone, m.p. 76° [from (II) and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in EtOH-NaOEt (trace)],

is similarly reduced to $\alpha\delta$ -dianisylhexan- γ -one, m.p. 69°, which with Zn-Hg-AcOH-fuming HCl gives $\alpha\delta$ -dianisylhexane, m.p. 53°, demethylated [boiling HI (*d* 1.7) in N_2] to $\alpha\delta$ -di-*p*-hydroxyphenylhexane, m.p. 98°. $\alpha\zeta$ -Dianisylhexane- $\alpha\zeta$ -dione, m.p. 146° (from adipyl chloride, PhOMe, and $AlCl_3$ in CS_2), is reduced (Clemmensen) to $\alpha\zeta$ -dianisylhexane, m.p. 71° (cf. van der Zanden, A., 1938, II, 181), which is demethylated to $\alpha\zeta$ -di-*p*-hydroxyphenylhexane, m.p. 143–144°. The product from anisaldazine and MgEtBr with Et_2O -HCl gives (III) and thence (IV). H. B.

Vitamin-E. XX. Preparation of *o*-xyloquinol. O. H. EMERSON and L. I. SMITH (J. Amer. Chem. Soc., 1940, 62, 141–142; cf. A., 1940, II, 13).—A 21% over-all yield of *o*-xyloquinone is obtained from *o*-xylene by way of the 3- NO_2 - (85% yield) and 3- NH_2 -derivative (75%). Reduction (Zn dust, aq. AcOH) then gives the quinol (95%). R. S. C.

Laccol. G. BERTRAND, H. J. BACKER, and N. H. HAACK (Bull. Soc. chim., 1939, [v], 6, 1670–1676; cf. A., 1933, 947; 1938, II, 183).—Mg hexadecyl bromide and 2:3:1-(OMe) $_2$ C $_6$ H $_3$ ·CHO give C $_{32}$ H $_{66}$, m.p. 68–70°, and 2:3-dimethoxyphenyl-*n*-hexadecylcarbinol, m.p. 55–56°, converted by $KHSO_4$ at 210° into 2:3-dimethyl-*n*- Δ^4 -heptadecenylbenzene, m.p. 47–47.5°, which is reduced (H_2 -Pt-black-AcOH) to 2:3-dimethoxy-*n*-heptadecylbenzene, m.p. 44.5–45°, identical with the dimethyltetrahydrolaccol of Majima (A., 1922, i, 262). Demethylation by HI (*d* 1.7)-AcOH with a little red P + PhOH then gives 2:3-dihydroxy-*n*-heptadecylbenzene, m.p. 63–64° (diacetate, m.p. 57.8–58.3°), identical with tetrahydrolaccol. Laccol is thus 2:3:1-(OH) $_2$ C $_6$ H $_3$ ·C $_{17}$ H $_{31}$ (cf. *loc. cit.*). A. T. P.

Structure of cannabidiol, a product isolated from the marihuana extract of Minnesota wild hemp. I. R. ADAMS, M. HUNT, and J. H. CLARK (J. Amer. Chem. Soc., 1940, 62, 196–200).—The high-boiling, physiologically active red oil, extracted by EtOH from the female tops of Minnesota wild hemp (*Cannabis sativa*; marihuana), contains ~33% of cannabidiol (I), C $_{21}H_{30}(32)O_2$, b.p. 187–190°/2 mm., [α] $^{25}_D$ –119° in 95% EtOH [*di*-*m*-nitrobenzenesulphonate, m.p. 119–120° (corr.); *Me* $_2$ ether, b.p. 175–177°/3 mm., [α] $^{25}_D$ –133° in 95% EtOH, obtained with difficulty; ? *Me* $_1$ ether, b.p. 177–179°/2 mm., [α] $^{25}_D$ –118° in 95% EtOH], isolated as *di*-3:5-dinitrobenzoate, m.p. 106–107° (corr.), [α] $^{27}_D$ –76° in COMe $_2$, and oxidised by $KMnO_4$ -NaHCO $_3$ in 50% aq. COMe $_2$ to *n*-hexoic acid. Colour reactions are described. (I) may be 2:3-dihydroxy-5'-methyl-5-*n*-amyl-2'-isopropenyl-3':4':5':6'-tetrahydrodiphenyl. R. S. C.

Vitamin-K-active derivatives of 2-methyl-1:4-naphthaquinol. S. ANSBACHER, E. FERNHOLZ, and M. A. DOLLIVER (J. Amer. Chem. Soc., 1940, 62, 155–158).—Prep. and the vitamin-K activity (1 unit given in parentheses below in μ g.) of the following are described. 2-Methyl-1:4-naphthaquinol diacetate (1), dipropionate (1), m.p. 74–75°, dibenzoate (1), m.p. 179°, *di*-*n*- (1.25), m.p. 52–53°, and *di*isobutyrate (5), m.p. 73–74°, *di*-*n*- (1.25), m.p. 40–41°, b.p. 210°/1 mm., and *di*iso-valerate (3), b.p. 185°/1 mm., and *Me* $_2$ ether (5), m.p. 48–49° (lit. 23–24°).

Antraquinone has -K activity (1 unit = ~2 mg.). These results and some aspects of the biological technique are discussed. R. S. C.

Water-soluble antihemorrhagic esters. L. F. FIESER and E. M. FRY (J. Amer. Chem. Soc., 1940, 62, 228–229).—The *K* $_2$ disulphate of dihydrovitamin-*K* $_1$ (i.e., the quinol) (I) and *Na* $_2$ 2:3-dimethyl-1:4-naphthaquinol disulphate, +2H $_2$ O, prepared by $ClSO_3H$ -C $_5$ H $_5$ N- CCl_4 , have no -K activity in 0.5 mg. doses, but *Na* $_2$ 2-methyl-1:4-naphthaquinol disulphate, +2H $_2$ O, is active in 2 μ g. doses and fairly successful clinically on intravenous injection. The diphosphoric acid (prepared by $POCl_3$ -C $_5$ H $_5$ N) of (I) is active in 25 (not 10) μ g. doses. *Na* $_4$ 2-methyl-1:4-naphthaquinol diphosphate, +2H $_2$ O, is also prepared. R. S. C.

Diacetate, m.p. 53.5–54.5°, of dihydrovitamin-*K* $_2$.—See A., 1940, III, 146.

Mechanism of the acid-catalysed dimerisation of anethole.—See A., 1940, I, 122.

Mode of reaction of organo-metallic compounds. IV. Rearrangement of diaryl ethers to *o*-arylphenols. A. LÜTTRINGHAUS and G. VON SÄÄF (Annalen, 1939, 542, 241–258; cf. A., 1938, II, 406; 1939, II, 109).—Ph $_2$ O and NaPh in C $_6$ H $_6$ at 50–72°/3–12 hr. give (after decomp. with MeOH and H $_2$ O) PhOH, *o*-C $_6$ H $_4$ Ph·OH (I) (main product), 2:6-diphenylphenol (II), b.p. 215–220°/11 mm., m.p. 101° (*Me*, m.p. 42°, and *Ph* ether, m.p. 119°), 2-phenoxydiphenyl (III), b.p. 200–201°/14 mm., m.p. 49.5°, and *di*-*o*-diphenyl ether (IV), m.p. 116°; little Ph $_2$ is produced. The intermediate formation of *o*-C $_6$ H $_4$ Na·OPh (V) is proved by treatment of the product from Ph $_2$ O and NaPh in C $_6$ H $_6$ at 6°/3 hr. with CO $_2$, whereby 10% of *o*-OPh·C $_6$ H $_4$ ·CO $_2$ H is obtained. NaPh and (III) in C $_6$ H $_6$ at room temp./3 hr. and then at 64°/6 hr. afford (I), (II), and (IV) but no PhOH. Possible reaction mechanisms are discussed; it is considered that (II) and (I) (as Na salts) arise by intramol. rearrangement of 3:1:2-C $_6$ H $_3$ NaPh·OPh and (V), respectively. *o*-C $_6$ H $_4$ Ph·OK and PhBr or *o*-C $_6$ H $_4$ PhI and KOPh with Cu powder at 210–220° give (III), which with conc. HNO $_3$ in AcOH at 100° (bath) affords a NO $_2$ -derivative, m.p. 149°, differing from 2-*p*-nitrophenoxydiphenyl, m.p. 87.5° (from *o*-C $_6$ H $_4$ Ph·OK and *p*-C $_6$ H $_4$ Br·NO $_2$). *m*-C $_6$ H $_4$ PhI and KOPh or *p*-C $_6$ H $_4$ Ph·OK and PhBr give 3-, b.p. 196–200°/14 mm., m.p. 14–16°, or 4-phenoxydiphenyl, b.p. 222°/14 mm., m.p. 68°, respectively. *o*-C $_6$ H $_4$ PhI and *o*-C $_6$ H $_4$ Ph·OK afford (IV). 4-Nitro-2:6-diphenylphenol, m.p. 136° [from CO(CH $_2$ Ph) $_2$ and NO $_2$ ·CNa(CHO) $_2$ in aq. EtOH-NaOH], is reduced (SnCl $_2$, Et_2O -HCl) to the NH $_2$ -derivative, m.p. (crude) 146–148°, which is deaminated (diazo-method) to (II). H. B.

Amines related to 2:5-dimethoxyphenylethylamine. I. R. BALTZLY and J. S. BUCK (J. Amer. Chem. Soc., 1940, 62, 161–164).—2:5:1-(OMe) $_2$ C $_6$ H $_3$ ·[CH $_2$] $_2$ ·NH $_2$ (hydrochloride, m.p. 139°), 36% aq. CH $_2$ O, and a little HCO $_2$ H at 125° (method A) give β -2:5-dimethoxyphenylethyldimethylamine, b.p. 159°/22 mm. (hydrochloride, m.p. 148°; methochloride, m.p. 184–185°). 2:5:1-(OMe) $_2$ C $_6$ H $_3$ ·COMe,

$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and $\text{Zn}\cdot\text{Cu}$ give $\text{Et } \beta\text{-2:5-dimethoxyphenylcrotonate}$, b.p. $140\text{--}143^\circ/1\text{ mm.}$ (derived acid, m.p. $113\cdot5^\circ$), reduced ($\text{H}_2\text{--PtO}_2$) to the ester, yielding $\beta\text{-2:5-dimethoxyphenyl-}n\text{-butyric acid}$, m.p. 79° . With dry NH_3 at $220\text{--}230^\circ$ this gives the amide, m.p. 121° , and thence (NaOCl ; 45% yield) $\beta\text{-2:5-dimethoxyphenyl-}n\text{-propylamine}$, b.p. $114^\circ/1\text{ mm.}$ (hydrochloride, m.p. $149\text{--}150^\circ$), which yields $\beta\text{-2:5-dimethoxyphenyl-}n\text{-propyl-methyl- (I) (hydrochloride, m.p. } 146^\circ$; hydriodide, m.p. 131°), and -dimethylamine [best prepared from (I) by method A] [hydrochloride, m.p. $182\text{--}183^\circ$; methochloride, m.p. ($+\text{H}_2\text{O}$) 92° and (anhyd.) $159\text{--}161^\circ$ (decomp.); methiodide, m.p. 139°]. The Et ester of 2:5-dimethoxybenzylidenemalonic acid, m.p. 183° (decomp.) [lit. 188° (decomp.)], is hydrogenated and then hydrolysed to 2:5-dimethoxybenzylmalonic acid, m.p. $156\cdot5^\circ$ (decomp.). 2:5-Dimethoxybenzylmethylmalonic acid, m.p. 143° (decomp.), at 150° gives $\beta\text{-2:5-dimethoxyphenylisobutyric acid}$, m.p. $59\cdot5^\circ$, the amide (II), m.p. 99° , of which is also obtained in poor yield by condensing 2:5:1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$, $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, and Zn , dehydrating by POCl_3 , hydrogenating, saponifying, etc. By a Hofmann reaction in aq. dioxan, (II) gives $\beta\text{-2:5-dimethoxyphenylisopropylamine}$, b.p. $137\text{--}140^\circ/3\text{ mm.}$ [hydrochloride, m.p. $117\cdot5^\circ$; hydriodide, m.p. 138° ; also obtained by hydrogenation of 2:5:1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$], and thence (Decker and method A) $\beta\text{-2:5-dimethoxyphenylisopropyl-methyl- (hydrochloride, m.p. } 98\cdot5^\circ$), and -dimethylamine, b.p. $118\text{--}121^\circ/0\cdot5\text{ mm.}$ (hydrochloride, m.p. $138\text{--}139^\circ$; methiodide, m.p. 142° ; hygroscopic methochloride, m.p. 203°). M.p. are corr.

R. S. C.

Dissociable organic oxides. Oxidation of 9:10-dihydroxy- and -dimethoxy-anthracene; influence of light. C. DUFRAISSE and R. PRIOT (Bull. Soc. chim., 1939, [v], 6, 1649—1656; cf. A., 1935, 1233; 1937, II, 145).—9:10-Dihydroxyanthracene (as Na_2 salt) and O_2 in the dark give only anthraquinone (I) (confirms result of Manchot, A., 1901, ii, 93). 9:10-Dimethoxyanthracene, insolated in CS_2 , quickly gives a photo-oxide, m.p. $144\text{--}145^\circ$ (block), transformed rapidly into (I) by heat or HI . Theoretical aspects are discussed.

A. T. P.

***p*-Aralkylaminophenols.**—See B., 1940, 118.

Hydrogenation of acetophenone to cyclohexylmethylcarbinol in the presence of solvent. V. N. IPATIEV and B. B. CORSON (J. Amer. Chem. Soc., 1939, 61, 3292).—With H_2 (100 kg./sq. cm.)— Ni-kieselguhr in $\text{iso-C}_5\text{H}_{12}$ at 100° , COPhMe gives 70% of cyclohexylmethylcarbinol (I), b.p. $189\cdot4\text{--}189\cdot8^\circ/761\text{ mm.}$, and 20% of PhEt ; at 75° it gives 92% of a $\sim 1:1$ mixture of (I) and $\text{CHPhMe}\cdot\text{OH}$ (II) and 8% of PhEt . With reduced Cu at 225° and no solvent, it gives 95% of PhEt , and in cyclohexane at 100° gives PhEt , (I), and (II).

R. S. C.

[Isomerisations of xanthophylls.] L. ZECHMEISTER, L. VON CHOLNOKY, and A. POLGÄR (Ber., 1939, 72 [B], 2039—2040; cf. A., 1939, II, 473).—A consideration of the authors' results in relationship to those of Strain (Carnegie Inst. Washington, Publ. 490).

H. W.

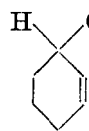
Diene synthesis. XI. Diene synthesis with vinyl esters and halogenated ethylenes. Simple route to the norcamphor series. K. ALDER and H. F. RICKERT (Annalen, 1939, 543, 1—27; cf. A., 1938, II, 488; 1939, II, 60).—cyclopentadiene (I) and $\text{CH}_2\text{:CH}\cdot\text{OAc}$ at $185\text{--}190^\circ$ give (mainly) Δ^5 -dehydronorbornyl acetate (II), b.p. $73\text{--}77^\circ/14\text{ mm.}$, and some impure 1:4:5:8-diendomethylene- Δ^6 -octahydro- β -naphthyl acetate (III), b.p. $140\text{--}145^\circ/14\text{ mm.}$; (II) is hydrolysed ($\text{MeOH}\text{--KOH}$) to Δ^5 -dehydronorborneol (IV), m.p. $108\text{--}109^\circ$ (adduct, $\text{C}_{13}\text{H}_{15}\text{ON}_3$, m.p. $147\text{--}148^\circ$, with PhN_3). Reduction (H_2 , Pt , AcOH) of (II) affords the acetate, b.p. $81\text{--}83^\circ/12\text{ mm.}$, of α -norborneol (V), m.p. $149\text{--}150^\circ$ (cf. A., 1935, 219; Komppa *et al.*, A., 1934, 1105) [also obtained by similar reduction of (IV); *H phthalate*, m.p. $109\text{--}110^\circ$; 3:5-dinitrobenzoate, m.p. 123° (compound, m.p. $139\text{--}140^\circ$, with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$); (V) is oxidised to norcamphor. The *H phthalate*, m.p. $80\text{--}81^\circ$ (cf. Komppa, 102—103°), and 3:5-dinitrobenzoate, m.p. 105° (compound, m.p. 126° , with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$), of β -norborneol are described. Oxidation ($\text{K}_2\text{Cr}_2\text{O}_7$, dil. H_2SO_4 , AcOH) of (IV) gives Δ^5 -dehydronorcamphor, f.p. $0\text{--}2^\circ$ (semicarbazone, m.p. $207\text{--}208^\circ$; adduct, $\text{C}_{13}\text{H}_{13}\text{ON}_3$, m.p. $140\text{--}141^\circ$, with PhN_3). The above production of (V) indicates that the OAc of (II) has the *endo*-configuration. Reduction (H_2 , PtO_2 , AcOH) and subsequent hydrolysis of (III) affords 1:4:5:8-diendomethylenedecahydro- β -naphthol, m.p. $90\text{--}92^\circ$ (acetate, b.p. $147\text{--}149^\circ/12\text{ mm.}$), which is not sterically homogeneous since it yields phenylcarbamates, m.p. 118° and $120\text{--}121^\circ$; it is oxidised to the 2-CO-derivative (A., 1939, II, 14). $\text{HCO}_2\text{:CH}\cdot\text{CH}_2$ and (I) at $180\text{--}190^\circ$ give dehydronorbornyl formate, b.p. $80^\circ/20\text{ mm.}$, and impure diendomethyleneoctahydro- β -naphthyl formate, b.p. $130\text{--}140^\circ/20\text{ mm.}$ $\text{CH}_2\text{:CH}\cdot\text{OAc}$ with $(\text{CH}_2\text{:CH})_2$, $(\text{CH}_2\text{:CMe})_2$, and $\Delta^{1:3}$ -cyclohexadiene at 180° affords the acetates of Δ^3 -cyclohexenol, 3:4-dimethyl- Δ^3 -cyclohexenol (phenylcarbamate, m.p. 112°), and 2:5-endoethylene- Δ^3 -cyclohexenol (phenylcarbamate, m.p. 125°), respectively; anthracene [in xylene at $220\text{--}230^\circ$ (autoclave)] gives 9:10-endoacetoxylethylene-9:10-dihydroanthracene, m.p. $100\text{--}101^\circ$, hydrolysed (25% $\text{MeOH}\text{--KOH}$) to the *OH*-derivative, m.p. $140\text{--}142^\circ$.

$\text{CH}_2\text{:CHCl}$ and (I) at $170\text{--}180^\circ$ yield a dehydronorbornyl chloride (VI), b.p. $46\text{--}47^\circ/12\text{ mm.}$ (adduct, $\text{C}_{13}\text{H}_{14}\text{N}_3\text{Cl}$, m.p. $113\text{--}116^\circ$, with PhN_3), and 2-chloro-1:4:5:8-diendomethylene- Δ^6 -octahydro-naphthalene, b.p. $128\text{--}130^\circ(?) /12\text{ mm.}$ (adduct, $\text{C}_{18}\text{H}_{20}\text{N}_3\text{Cl}$, m.p. 195° , with PhN_3). Reduction (H_2 , $\text{Pd}\text{--CaCO}_3$, EtOAc) of (VI) gives norbornyl chloride, b.p. $50\text{--}52^\circ/11\text{ mm.}$ (Komppa *et al.*, loc. cit.) (the *Mg* derivative of which with CO_2 affords 2:5-endomethylenehexahydrobenzoic acid, b.p. $128\text{--}130^\circ/12\text{ mm.}$), reduced (Na , EtOH) to norbornylane and converted by boiling quinoline into norbornylene. $(\text{CHCl})_2$ reacts more slowly with (I) at $180\text{--}190^\circ$ and gives 1:2-dichloro-3:6-endomethylene- Δ^4 -cyclohexene, b.p. $70\text{--}76^\circ/11\text{ mm.}$ (adduct, $\text{C}_{13}\text{H}_{13}\text{N}_3\text{Cl}_2$, decomp. 148° , with PhN_3), and 2:3-dichloro-1:4:5:8-diendomethylene- Δ^6 -octahydronaphthalene, b.p. $140\text{--}150^\circ/11\text{ mm.}$ [adduct, $\text{C}_{18}\text{H}_{19}\text{N}_3\text{Cl}_2$, m.p. 210° (decomp.), with PhN_3]. $\text{CHCl}_2\cdot\text{CCl}_2$ and (I) at $175\text{--}185^\circ$ afford a 1:2 adduct, b.p. $158\text{--}160^\circ/11\text{ mm.}$

(adduct, $C_{18}H_{18}N_3Cl_3$, m.p. 225—226°, with PhN_3). The diene synthesis has now been shown to occur with all types (classified) of olefines; there are considerable differences in the rates of addition.

H. B.

Olefine peroxides. R. CRIEGEE, H. PILZ, and H. FLYGARE (Ber., 1939, 72, [B], 1799—1804; cf. A., 1937, II, 59; Hock *et al.*, A., 1938, II, 360).—The purest samples of cyclohexene peroxide (I) are obtained by shaking the hydrocarbon with O_2 for a relatively short time in a SiO_2 flask irradiated by ultra-violet light at 35° and immediate working up of the product. The best specimens have b.p. 51°/0.3 mm. but it is unlikely that they are quite homogeneous. The constitution (A) for (I) is supported by the following arguments. (I) is smoothly reduced to cyclohexenol (II). Acids transform (I) mainly into a mixture of stereoisomeric cyclohexanetriols obtained by hydration of a cyclohexenol oxide formed by O displacement.



(A.)

Cone. alkalis transform (I) into (II) by reduction and into a mixture of acids (mainly α -hydroxyadipic acid) by oxidation; by-products are also formed. The presence of a double linking in (I) is established by the absorption of 2 Br when (I) is titrated with aq. KBr— $KBrO_3$ or treated with Br in AcOH or CCl_4 . With $MgMeI$, (I) evolves ~90% of the calc. vol. of CH_4 . $Pb(OAc)_4$ reacts vigorously with cold (I); this change is studied in detail with tetrahydronaphthalene peroxide. It occurs only when O_2H is present [ascaridole is unattacked by $Pb(OAc)_4$] and appears suited to the determination of O_2H . The physical consts. of (I) are in agreement with (A). A contrary argument is found in the formation of greater or smaller amounts of *trans*-cyclohexanediol, adipic acid, and cyclopentenealdehyde in the second and third of the above changes. cyclopentene peroxide, b.p. 35°/0.01 mm., is prepared similarly; it is reduced to Δ^2 -cyclopentenol, b.p. 140°/747 mm. (phenylurethane, m.p. 121.5°). 1-Methylcyclohexene peroxide, b.p. 47—51°/0.01 mm., similarly yields 2-methyl- Δ^2 -cyclohexenol (phenylurethane, m.p. 204.5°). α -Pinene is very slowly autoxidised. Co oleate causes rapid absorption of O_2 but accelerates decomp. as well as formation of the peroxide. Olefines with terminal double linking react still more slowly; camphene and Δ^2 -*n*-heptene absorb only a few c.c. in 24 hr. 1-Ethoxycyclohexene absorbs O_2 avidly but the primary peroxide appears to lose EtOH so that a homogeneous product cannot be obtained.

H. W.

Peroxide of cymene. A. VON REBAY and H. FERTBACK (Ber., 1939, 72, [B], 1643—1645).—Prolonged passage of O_2 through cymene at 60° gives the liquid cymene peroxide, $C_{10}H_{14}O_2$, best isolated through the Na salt obtained with 35% NaOH. It begins to decompose at 100° with weak evolution of gas and formation of a yellow colour and passes at 220° into a dark red oil. It immediately causes the typical red luminescence when added to Mg phthalocyanine in boiling PhCl and this persists for a considerable time. It liberates I from warm, acid KI solution. Its characteristic odour disappears rapidly when it is boiled with (preferably alkaline) H_2O and is re-

placed by that of cuminaldehyde, identified as its semicarbazone and by conversion into cuminic acid.

H. W.

Synthesis of compounds related to the anti-rachitic vitamins. II. J. B. ALDERSLEY, G. N. BURKHARDT, A. E. GILLAM, and N. C. HINDLEY (J.C.S., 1940, 10—16; cf. A., 1938, II, 234).—Quinitol monoacetate, m.p. 68—72°, b.p. 136—137°/15 mm., prepared by hydrolysis (KOH—EtOH) of the diacetate, is oxidised (H_2CrO_4 —AcOH) (as is quinitol by CrO_3 — Ac_2O) to 4-acetoxycyclohexanone, b.p. 112—114°/11 mm., 235°/760 mm., hydrolysed (NaOH) to the OH-compound (I), b.p. 83—85°/0.6 mm., and with $PhCHO$ — $AcOH$ —HCl forming 4-acetoxy-2:6-dibenzylidenecyclohexanone, m.p. 165°. cyclohexylideneacet-aldehyde [prep. from 1-allylcyclohexanol (3:5-dinitrobenzoate, m.p. 101—103°)] and (I) in 0.086N-NaOH and N_2 give a mixture containing chiefly 5-hydroxy-2-keto- α - β -dicyclohexylidene-ethane (II), m.p. 65—69°, the acetate, m.p. 80—82° (2:4-dinitrophenylhydrazones, m.p. 187—189°), of which with CH_2Br — CO_2Et and Zn in C_6H_6 and N_2 yields a product, converted by successive hydrolysis (MeOH—KOH), dehydration (Ac_2O), hydrolysis, and decarboxylation into a hydroxytriene (III), $C_{15}H_{22}O$ (unstable phenylurethane, m.p. 123—132°), which appears to be a mixture of isomerides and is also prepared from (II) and $MgMeI$ (excess); the predominant isomeride is considered to be α -cyclohexylidene- β -5-hydroxy-2-methyl- Δ^2 -cyclohexenylidene-ethane. There is a considerable difference between the absorption max. of calciferol and (III).

Reduction [$Al(OPr^s)_3$, Pr^sOH] of (II) gives a compound, $C_{14}H_{20}O$, m.p. 81—83°, presumably α -cyclohexylidene- β -3-hydroxy- Δ^5 -cyclohexenylidene-ethane.

F. R. S.

6-Benzoyloxyhydrind-1-ol. M. MIYASAKA (J. Pharm. Soc. Japan, 1939, 59, 119—121).—6-Hydroxyhydrind-1-one (I) is reduced by Na and EtOH to 6-hydroxyhydrind-1-ol, m.p. 121°, in poor yield. (I) is therefore transformed by $BzCl$ and C_5H_5N into 6-benzoyloxyhydrind-1-one, m.p. 141°, which is reduced catalytically to 6-benzoyloxyhydrind-1-ol, m.p. 111°. This has no activity in the Allen-Doisy test even with a max. injection of 99 μg . It may therefore be considered that the five-membered ring constituting part of the α estrone nucleus does not participate in oestrogenic activity and that α estrone does not decompose in the body with formation of a hydrindene derivative.

H. W.

Reaction between 2:3-dimethyl-1:4-naphthaquinone and magnesium phenyl bromide. II. (Miss) H. M. CRAWFORD (J. Amer. Chem. Soc., 1939, 61, 3310—3314).—The compounds, m.p. 203—204° and 208—209°, obtained (A., 1935, 1501) by addition of 2 $MgPhBr$ to 2:3-dimethyl-1:4-naphthaquinone (I) are 1:4-dihydroxy-1:4-diphenyl-2:3-dimethyl-1:4-dihydronaphthalene (II) and 1:4-dihydroxy-1:2-diphenyl-2:3-dimethyl-1:2-dihydronaphthalene (III), respectively. Both have 2 active H ($MgMeI$). (II) is also obtained from (I) (20%) or 1-hydroxy-4-keto-1-phenyl-2:3-dimethyl-1:4-dihydronaphthalene (IV) (50% yield) by 2 $LiPh$. Boiling CrO_3 —AcOH (not $KMnO_4$ and less well $K_2Cr_2O_7$) with (II) gives o - $C_6H_4(COPh)_2$, proving the structure. 1-Keto-2:4-

diphenyl-2 : 3-dimethyl-1 : 2-dihydronaphthalene (V), m.p. 124°, is obtained (once only) by recrystallising the double compound of (I) and (II) and quantitatively by dehydrating (II) with HCl-MeOH or ZnCl₂-HCl-C₆H₆, its structure (and the rearrangement) being proved by its oxidation by K₂Cr₂O₇-AcOH to C₆H₅Me and *o*-C₆H₄Bz·CO₂H. With MgPhBr or LiPh, (V) gives a metallic compound, decomposed by H₂O to 1-hydroxy-1 : 2 : 4-triphenyl-2 : 3-dimethyl-1 : 2-dihydronaphthalene (VI), m.p. 164—174°, or by acid to 1 : 1 : 4-triphenyl-3-methyl-2-methylene-1 : 2-dihydronaphthalene (VII), m.p. 189—190° [also obtained by ZnCl₂-HCl-C₆H₆ from (VI); adds Br]. (VII) is stable to COMe₂-KMnO₄ at room temp. and with K₂Cr₂O₇-AcOH gives only a little BzOH and an oil, but with O₃ in CHCl₃ or CCl₄ gives mainly 2-keto-1 : 1 : 4-triphenyl-3-methyl-1 : 2-dihydronaphthalene (VIII), m.p. 228°, and CH₂O. Oxidation of (VIII) to α -diphenylhomophthalic acid (*Me* ester, m.p. 192—193°) and its interaction with MgMeI to regenerate (VII) prove the structure of (VI), (VII), and (VIII). (III) is obtained also from (IV) by MgPhBr, is oxidised (K₂Cr₂O₇-AcOH) to C₆H₅Me and *o*-C₆H₄Bz·CO₂H (proof of structure), is dehydrated by PBr₃ in CHBr₃ at 100°, C₆H₆-ZnCl₂-HCl, or hot I-AcOH (not 20% H₂SO₄ or Ac₂O-NaOAc) to 4-keto-1 : 1-diphenyl-2 : 3-dimethyl-1 : 4-dihydronaphthalene (cf. *loc. cit.*), m.p. 183°. This gives no CO-derivatives, is stable to K₂Cr₂O₇- and CrO₃-AcOH, KMnO₄-KOH, 30% H₂O₂, O₃, and Br; with Zn-AcOH it gives a small amount of a substance, C₂₄H₂₂O, m.p. 142—143°, and a hydrocarbon, m.p. 176—177°; it adds 1 MgMeI and contains no active H; with MgPhBr or LiPh it gives a metallic compound, decomposed by aq. NH₄Cl to 4-hydroxy-1 : 1 : 4-triphenyl-2 : 3-dimethyl-1 : 4-dihydronaphthalene (IX), m.p. 154°, or by acid to (VII) [also obtained by dehydrating (IX) by melting or by ZnCl₂-HCl-C₆H₆]. (IX) shows 1 active H, is stable to KMnO₄, and with O₃ gives (VIII), probably by way of (VII). Many of the above-mentioned oxidations give also small amounts of a hydrocarbon, C₃₀H₄₂, m.p. 235°, converted by O₃ into an oil.

R. S. C.

Amines related to 2 : 5-dimethoxyphenylethylamine. II. R. BALTZLY and J. S. BUCK (J. Amer. Chem. Soc., 1940, 62, 164—167).—Et β -2 : 5-dimethoxyphenylpropionate, b.p. 164—167°/1 mm., obtained in 80% yield by the Reformatsky reaction, gives the *hydrazide*, m.p. 161.5°, and thence (Curtius) 5-2' : 5'-dimethoxyphenyloxazolid-2-one, m.p. 107°, and (cold, conc. HCl) β -hydroxy- β -2 : 5-dimethoxyphenylethylamine (III) (as *hydrochloride*, m.p. 158.5°). 2 : 5 : 1-(OMe)₂C₆H₃·CO·CH₂Br (IV) and (CH₂)₆N₄ give ω -amino-2 : 5-dimethoxyacetophenone *hydrobromide*, m.p. 195° (decomp.), reduced (H₂-PtO₂) to (III). NHMe·CH₂Ph and (IV) in Et₂O give 2 : 5-dimethoxyphenylbenzylmethylamine (V) (as *hydrochloride*, m.p. 167.5°), reduced (H₂-PtO₂ in EtOH) to PhMe and β -hydroxy- β -2 : 5-dimethoxyphenylethylmethylamine *hydrochloride*, m.p. 151.5°. MgMeI and (V) with subsequent hydrogenation give β -hydroxy- β -2 : 5-dimethoxyphenyl-*n*-propylmethylamine *hydrochloride*, m.p. 158—159°. Crude Et β -hydroxy- β -2 : 5-dimethoxyphenyl-*n*-butyrate [prepared from 2 : 5 : 1-(OMe)₂C₆H₃·COMe, CH₂Br·CO₂Et, and Zn-Cu; de-

rived acid, m.p. 121—122°] gives the *hydrazide*, m.p. 112°, and thence (as above) 5-2' : 5'-dimethoxyphenyl-5-methyloxazolid-2-one, m.p. 159°, and β -hydroxy- β -2 : 5-dimethoxyphenyl-*n*-propylamine *hydrochloride*, m.p. 174°. 1 : 4 : 2-(OMe)₂C₆H₃·MgBr and NMe₂·CH₂·CN give ω -dimethylamino-2 : 5-dimethoxyacetophenone (VI), the *hydrochloride*, m.p. 171° (decomp.), of which is hydrogenated (PtO₂) in EtOH to β -hydroxy- β -2 : 5-dimethoxyphenylethylmethylamine *hydrochloride*, m.p. 155° (corresponding *methochloride*, m.p. 185—186°). MgMeI converts (VI) into β -hydroxy- β -2 : 5-dimethoxyphenyl-*n*-propyldimethylamine (*hydrochloride*, m.p. 176.5°; *methochloride*, m.p. 213.5°). α -Oximino-2 : 5-dimethoxypropiphenone, m.p. 97—98°, and H₂-Pd-C in abs. EtOH-HCl give β -hydroxy- β -2 : 5-dimethoxyphenylisopropylamine *hydrochloride*, m.p. 175—176° (decomp.). 2 : 5 : 1-(OMe)₂C₆H₃·CO·CHMeBr (prep. from COArEt by Br in CHCl₃) and NH₂Me in abs. Et₂O at 0° give a salt, converted into α -methylamino-2 : 5-dimethoxypropiphenone *hydrochloride*, m.p. 172—173° (decomp.), hydrogenation of which yields β -hydroxy- β -2 : 5-dimethoxyphenylisopropylmethylamine *hydrochloride*, m.p. 170°; NHMe₂ gives similarly α -dimethylamino-2 : 5-dimethoxypropiphenone *hydrochloride*, m.p. 154—156° (decomp.), and β -hydroxy- β -2 : 5-dimethoxyphenylisopropylmethylamine [*hydrochloride*, m.p. 198° (decomp.); *methochloride*, m.p. 221—223° (decomp.)]. M.p. are corr.

R. S. C.

Action of sodium nitrite on Michler's hydrol in hydrochloric acid. A. C. HUTCHISON and T. H. READE (J.C.S., 1940, 93—96).—NaNO₂ (4 mols.) and (*p*-NMe₂·C₆H₄)₂CH·OH (1 mol.) in excess of 4.8N-HCl at 0° give *p*-NO₂·C₆H₄·NMe·NO, *p*-NO·NMe·C₆H₄·CHO, *p*-NO₂·C₆H₄·NMe₂, *p*-NO·C₆H₄·NMe₂, and 3 : 4 : 1-NO₂·C₆H₃(NMe₂)·CHO, with CH₂O and NO. In 1.2N-HCl the reaction is the same but the relative amounts of the products are altered. Equations are put forward to interpret schematically the course of the reaction. F. R. S.

Dark reaction following photolysis of malachite-green leucocyanide.—See A., 1940, 1, 124.

Synthesis in the steroid series. E. DANE (Angew. Chem., 1939, 52, 655—659).—A review.

Catalytic hydrogenation of 5 : 6-dibromides of sterols. J. DECOMBE and J. RABINOWITCH (Bull. Soc. chim., 1939, [v], 6, 1510—1522).—Hydrogenation (Pt-aq. Et₂O) at normal temp. and pressure is used in attempts to prove the structure of dihalogeno-compounds (cf. Vavon *et al.*, A., 1938, II, 323). Efficiency of catalyst is quickly impaired with Cl-, which are less reactive than the corresponding Br-compounds. Addition of halogen to the double linking of cholestene affords four possible stereoisomerides. β -Cholestene dibromide (I), m.p. 106°, is converted partly into the α -form (II), new m.p. 148°, by AgNO₃, KOAc, Zn(OAc)₂, or NaOH in EtOH, or by prolonged boiling in EtOH. Irradiation (240 hr.) of (I) in light petroleum gives a little (II) and 50% of γ -dibromide (III), m.p. 116—117°, [α] -40.1° to +38.6° (in CHCl₃; 10 days) (cf. Mauthner, A., 1906, i, 663), probably intermediate in the conversion of (I) into (II). (I) and (III) on hydrogenation lose 2 Br, and their

structures cannot be determined. Cholestene dichloride, new m.p. 121—122°, and (II) are not hydrogenated. Cholesterol dibromide (IV) (best method of prep.: Windaus, A., 1906, i, 174), $[\alpha]_{578}^{25}$ —50° in CHCl_3 , or dichloride (V), m.p. 136—137°, and CrO_3 -AcOH at 55° give $\Delta^{5:6}$ -cholestenone dibromide (VI), $[\alpha]_{578}^{25}$ —55.8° in CHCl_3 , or dichloride (VII), m.p. 110—111° (block), softens 108° (slow heating), $[\alpha]_{578}^{25}$ —30° in CHCl_3 , respectively. (IV) or (VI) loses 2 Br (the latter with migration of double linking to 4:5) and gives cholesterol or cholestenone, respectively. Hydrogenation of (V) or (VII) causes successive replacement of Cl [in the case of (VII), CO is reduced first] to give (?) 6-chlorocholestanols, m.p. 136—137°, $[\alpha]_{587}^{25}$ —16.6° in CHCl_3 (also +1H₂O, m.p. 120° and then 126—128°) (cf. de Fazi *et al.*, A., 1932, 510), and (less readily formed) m.p. 94°, $[\alpha]_{578}^{25}$ —16.6° in CHCl_3 , respectively, and finally in either case, β -cholestanol. Structural formulæ are discussed.

A. T. P.

Fission of cholesterol oxide. J. HATTORI (J. Pharm. Soc. Japan, 1939, 59, 129—131).—Cholesteryl acetate and H₂O₂ give 5-hydroxy-3:6-diacetoxycholestane (I) and 3:5:6-triacetoxycholestane (II), m.p. 148—149.5°, also obtained from (I) by Ac₂O-HCl. MeOH-KOH hydrolyses (II) to 3:6-dihydroxy-5-acetoxycholestane (III), m.p. ~170°, which with MeOH-H₂SO₄ gives 3:6-dihydroxy-5-methoxycholestane (IV), m.p. 203—204° (diacetate, m.p. 113—114°). Cleavage of α - or β -cholesterol oxide acetate by AcOH yields (I). With MeOH-H₂SO₄ the α -oxide gives 3:5-dihydroxy-6-methoxycholestane, m.p. 151—152.5° (3-acetate, m.p. 139.5—140.5°), and the β -oxide gives (IV). CrO₃ oxidises (III) to 5-acetoxycholestane-3:6-dione, m.p. 165.5—167°, whence KOH-MeOH yields Δ^4 -cholestene-3:6-dione.

R. S. C.

7-Dehydroepicholesterol. A. WINDAUS and J. NAGGATZ (Annalen, 1939, 542, 204—218).—epi-Cholesteryl acetate (Ruzicka *et al.*, A., 1937, II, 65) is oxidised (CrO₃-AcOH) to (impure) 7-ketoepicholesteryl acetate (I), m.p. 119° (absorption max. at 234 m μ), and (probably) a 5-hydroxy-6-keto-3-acetoxy- Δ^3 -cholestene (II), m.p. 163°. Hydrolysis (1% MeOH-NaOH) of (II) gives Δ^4 -cholestene-3:6-dione [monophenylhydrazones, m.p. 272°; disemicarbazone, also obtained directly from (II)], which is also formed by adsorption of (II) on Al₂O₃. Freshly ignited Al₂O₃ converts (I) into $\Delta^{3:5}$ -cholestadien-7-one; incomplete purification is effected with Al₂O₃ which has been kept in air for 2 weeks. Reduction [Al(OPrⁱ)₃, PrⁱOH] of (I) and subsequent hydrolysis (MeOH-KOH) gives α -, m.p. 172—176°, $[\alpha]_{\text{D}}^{25}$ +38.1°, and β -, m.p. 173°, $[\alpha]_{\text{D}}^{25}$ +9.1°, 7-hydroxyepicholesterol which differ in the steric arrangement at C₇, and are purified through their diacetates, m.p. 165°, $[\alpha]_{\text{D}}^{25}$ +20.2°, and m.p. 145°, $[\alpha]_{\text{D}}^{25}$ +70.2°, respectively (separated by fractional adsorption on Al₂O₃). Decomp. of the α -dibenzoate, m.p. 154°, $[\alpha]_{\text{D}}^{25}$ +93.7°, at 200° affords $\Delta^{3:5:7}$ -cholestatriene (III), but the β -dibenzoate, non-cryst., m.p. 70—80°, $[\alpha]_{\text{D}}^{25}$ +10.7°, at 195°/high vac. or, less well, in boiling NPhMe₂ gives a little (III) and (mainly) the benzoate, m.p. 118—119°, $[\alpha]_{\text{D}}^{25}$ +48.5°, of 7-dehydroepicholesterol (IV), m.p. 124—126°, $[\alpha]_{\text{D}}^{25}$ —70.5° (acetate, m.p. 114—115°, $[\alpha]_{\text{D}}^{25}$ —35°) [spec-

trum similar to that of 7-dehydrocholesterol (V)]. Changes in absorption spectra show that decomp. of ergosterol and (IV) during irradiation (Hg light) occurs in the same way at the same rate. The product obtained by irradiation (Mg arc) of (V) is about 10 times as active as that similarly formed from (IV). $[\alpha]$ are in CHCl_3 .

H. B.

Dehydrocholestenone and its hydrogenation with aluminium isopropoxide. A. WINDAUS and O. KAUFMANN (Annalen, 1939, 542, 218—224).—7-Dehydrocholesterol is oxidised [Al(OBuⁱ)₃, COMe₂, C₆H₆] to dehydrocholestenone (I), m.p. 88°, $[\alpha]_{\text{D}}^{25}$ +34° in CHCl_3 [semicarbazone, m.p. 240° (decomp.)], which may be the $\Delta^{4:5:7:8}$ or $\Delta^{4:5:8:14}$ derivative. Reduction [Al(OPrⁱ)₃, PrⁱOH] of (I) gives a mixture of 35.25, 48.75, 14.75, and 1.25%, respectively, of aldehydecholesterol (+xH₂O) (II), m.p. 115—116°, $[\alpha]_{\text{D}}^{25}$ +10° in CHCl_3 (acetate, m.p. 109°, $[\alpha]_{\text{D}}^{25}$ —56° in CHCl_3 ; 3:5-dinitrobenzoate, double m.p. 154° and 180—185°, $[\alpha]_{\text{D}}^{25}$ —78.5° in CHCl_3), aldehydecholesterol (III), m.p. 93—94°, $[\alpha]_{\text{D}}^{25}$ +80° in CHCl_3 (acetate, m.p. 96°, $[\alpha]_{\text{D}}^{25}$ +126.3° in CHCl_3 ; 3:5-dinitrobenzoate, double m.p. 150° and 180—185°, $[\alpha]_{\text{D}}^{25}$ +159° in CHCl_3), 7-dehydrocholesterol (IV), and 7-dehydroepicholesterol (V). (II) + (IV) are pptd. by digitonin. (II) and (III) are separated from (IV) and (V), respectively, by adsorption on silicic acid and fractional elution. The amounts of (IV) and (V) are determined spectrophotometrically.

H. B.

Preparation of $\Delta^{4:6}$ -cholestadien-3(β)-ol. V. A. PETROW (J.C.S., 1940, 66—67).—Reduction of $\Delta^{4:6}$ -cholestadien-3-one (I) (2:4-dinitrophenylhydrazones, m.p. 231—233°) with Al(OPrⁱ)₃ in PrⁱOH gives an additive complex, m.p. 113°, of $\Delta^{4:6}$ -cholestadien-3(β)-ol (II), m.p. 126—127°, $[\alpha]_{\text{D}}^{25}$ —38.0° in CHCl_3 , and its epimeride, from which (II) is pptd. as digitonide. The acetate of (II) has m.p. 78—79°, $[\alpha]_{\text{D}}^{25}$ —71.6° in CHCl_3 . Oxidation of (II) with Al(OBuⁱ)₃ in COMe₂-C₆H₆ yields (I). The (II) of Dane *et al.* (A., 1937, II, 417) was largely contaminated with cholesterol.

F. R. S.

Deoxycholamine. W. T. CALDWELL (J. Amer. Chem. Soc., 1939, 61, 3584—3585).—Deoxycholhydrazide gives an azide, which by decomp. in aq. AcOH at 45—60°, followed by warming with KOH-EtOH, gives deoxycholamine, +MeOH, m.p. (MeOH-free) 157—158° (hydrochloride, sinters at 300°, m.p. 306°), which may be a stereoisomeride of that described by Vanghelovici (A., 1939, II, 546).

R. S. C.

Sterols. LXXXI. Conversion of sarsasapogenin into pregnane-3(α):20(α)-diol. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 3592—3593).—Heating with Ac₂O at 200° and subsequent hydrolysis converts sarsasapogenin into ψ -sarsasapogenin, m.p. 171—173°, oxidised by CrO₃-AcOH to an unsaturated diketone, C₂₁H₃₀O₂, m.p. 201—203°, which is reduced by Na-EtOH to pregnane-3(α):20(α)-diol. This is the best source of hormones of this series.

R. S. C.

$\Delta^{5:16}$ -Pregnadiene-3:20-diol. A. BUTENANDT and J. SCHMIDT-THOMÉ (Ber., 1939, 72, [B], 1960—1962).— Δ^5 -Pregnene-3:17:20-triol 3:20-diacetate is converted by POCl₃ in boiling C₅H₅N into $\Delta^{5:16}$.

pregnadiene-3:20-diol 3:20-diacetate (I), m.p. 121°, which is hydrolysed (NaOH-aq. MeOH) to $\Delta^{5,16}$ -*pregnadiene-3:20-diol* (II), m.p. 168—170°, re-converted by $\text{Ac}_2\text{O}-\text{C}_6\text{H}_5\text{N}$ at room temp. into (I). Hydrogenation (PtO_2 in AcOH) of (II) gives *allo-pregnane-3(β):20(β)-diol*, m.p. 193° (*acetate*, m.p. 138°), oxidised (CrO_3 in AcOH) to *allopregnane-3:20-dione*. (II) is devoid of androgenic activity.

H. W.

Sterols. LXXVII. Oxidation of pregnane-3:4:20(α)-triol and of coprostanone-3:4-diol. R. E. MARKER, E. L. WITTLE, L. PLAMBECK, jun., E. ROHRMANN, J. KRUEGER, and P. R. ULSHAFFER (J. Amer. Chem. Soc., 1939, 61, 3317—3320).—The point of cleavage of ring A of sterols depends on the substituent at C₁₇. CrO_3 attacks mainly the 2:3-linking of coprostanone (cf. Gardner *et al.*, A., 1914, i, 169). $\text{H}_2-\text{PtO}_2-\text{EtOH}-\text{Et}_2\text{O}$ at 3 atm. reduces 4:20-diacetoxypregnan-3-one (I), m.p. 250°, to 4:20-diacetoxypregnan-3-ol, m.p. indefinite, hydrolysed by KOH-EtOH to *pregnane-3:4:20(α)-triol* (II), m.p. 184° [no digitonide; *triacetate*, m.p. 181°, obtainable also by reduction of (I) by $\text{Al}(\text{OPr}^i)_3-\text{Pr}^i\text{OH}$ and subsequent acetylation], and oxidised by CrO_3 in 95% AcOH at 25° to a 3:4-diacid (III), $\text{C}_{21}\text{H}_{32}\text{O}_5$, m.p. 216° (*oxime*, m.p. 238°). This acid differs from the 2:3-diacid, m.p. 281° (Me_2 ester, m.p. 87°), obtained (Butenandt, A., 1930, 633, m.p. 270°) by oxidation of pregnanedione. $\text{Pb}(\text{OAc})_4$, followed by H_2O_2 , oxidises (II) to an acid, $\text{C}_{21}\text{H}_{34}\text{O}_5$, m.p. 231°, converted into (III) by CrO_3 . 4-Bromocoprostanone and KOAc-AcOH give 4-acetoxycoprostanone, m.p. 149°, which with $\text{H}_2-\text{PtO}_2-\text{EtOH}-\text{Et}_2\text{O}$ at 3 atm., followed by KOH-EtOH, gives *coprostanone-3:4-diol*, m.p. 185—188° (? and an isomeride), oxidised by CrO_3 -AcOH at room temp. to a 3:4-dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$, m.p. 217° (Me_2 ester, m.p. 74°).

R. S. C.

Ketones. I. Condensation of ketones with cyanoacetic acid. M. M. SCHEMJAKIN and D. M. TRACHTENBERG (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 763—767).—*cyclo*-Pentanone or -hexanone and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) + excess of piperidine at 100—105° for 2 hr. give *cyclo*-pentenyl- or -hexenyl-acetonitrile, respectively. COMe_2 or COMeEt similarly, at 110—115°, gives $\text{CMe}_2\text{CH}\cdot\text{CN}$ or $\text{CMeEtCH}\cdot\text{CN}$, respectively. α -Hydrindone (II) affords 3-indenylacetonitrile, m.p. 68—70° [that, m.p. 18°, described by Ingold *et al.* (J.C.S., 1919, 115, 143) is probably an isomeride]; oxidation (KMnO_4) gives no (II). The catalyst is probably the piperidine salt of (I). COPhMe or COPh_2 and (I) do not react as above.

A. T. P.

Asymmetric reduction of β -methylcinnamic acid by d -glucose in presence of Raney nickel. T. D. STEWART and D. LIPKIN (J. Amer. Chem. Soc., 1939, 61, 3297—3300).—Reduction of $\text{CPhMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ by glucose in aq. KOH in presence of Raney Ni is up to 0.5% asymmetric, $[\alpha]_{5461}$ of the product varying from +0.31° to -0.42° according to the conditions. The reaction mechanism is discussed.

R. S. C.

Preparation and asymmetric reduction of β -methylcinnamic acid. D. LIPKIN and T. D. STEWART (J. Amer. Chem. Soc., 1939, 61, 3295—

3296).—Hydrogenation (PtO_2 ; EtOH) of the hydro-cinchonine salts of $\text{CPhMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (improved preps.) causes partial asymmetric formation of the saturated acids (cf. Erlenmeyer, A., 1930, 1433).

R. S. C.

Restricted rotation in arylolefines. I. Preparation and resolution of β -chloro- β -3-bromo-2:4:6-trimethylphenyl- α -methylacrylic acid. R. ADAMS and M. W. MILLER (J. Amer. Chem. Soc., 1940, 62, 53—56).—The structure of *bromopropiomesitylene* (I), b.p. 127—129°/3 mm., prepared from 1:3:5:2- $\text{C}_6\text{H}_2\text{Me}_3\text{Br}$, (EtCO)₂O, and AlCl_3 in CS_2 , is proved by fission by boiling syrupy H_3PO_4 and nitration of the product to give 1:3:5:2:4:6- $\text{C}_6\text{Me}_3\text{Br}(\text{NO}_2)_2$, m.p. 199.5—201.5° (lit. 189—190°). MgEtBr in Et_2O converts (I) into the MgBr derivative of the enolic form, carbonated to give α -3-bromo-2:4:6-trimethylbenzoylpropionic acid, m.p. 123—124° (decomp.), in 51% yield. With $\text{PCl}_5\text{-POCl}_3$ at 100° (bath) this gives β -chloro- β -3-bromo-2:4:6-trimethylphenyl- α -methylacrylic acid (II) (53%), m.p. 157—158°. Quinine in abs. EtOH resolves this into the *d*- and *l*-acids, m.p. 155—156°, $[\alpha]_D^{20} +69.4^\circ$, -54° in abs. EtOH, respectively (*quinine* salts, cryst., $[\alpha]_D^{20} -46.8^\circ$ in abs. EtOH, and an oil, respectively). Br converts the *d*-, *l*-, and *dl*-acids into the same inactive β -chloro- β -3:5-dibromo-2:4:6-trimethylphenyl- α -methylacrylic acid, m.p. 228—229°, but ClSO_3H at -10° gives β -chloro- β -3-bromo-5-chlorosulphonyl-2:4:6-trimethylphenyl- α -methylacrylic acid, m.p. 183—184°, $[\alpha]_D^{20} -8.6^\circ$, m.p. 183—184°, $[\alpha]_D^{20} +10.0^\circ$ in C_6H_6 , and m.p. 188—189°, α , 0, respectively. M.p. are corr.

R. S. C.

Synthesis of phenylalanine from benzylmalonic and benzylcyanoacetic esters through the phenylhydrazone of phenylpyruvic acid. V. FEOFILAKTOV and E. VINOGRADOVA (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 759—760).— $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and $\text{PhN}_2\cdot\text{OK}$ at 0° afford (probably) Et benzeneazo-benzylmalonate, converted by aq. EtOH-alkali into $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ (60%), also obtained (30%) similarly from Et benzylcyanoacetate.

A. T. P.

Preparation of monoalkylaminoalkyl amino-benzoates. S. D. GOLDBERG, W. F. RINGK, and P. E. SPOERRI (J. Amer. Chem. Soc., 1939, 61, 3562—3564).— $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$ and NH_2R (excess) in boiling H_2O or 95% EtOH give ~52% of β -methyl-, b.p. 142—143° (*picrate*, m.p. 137—138°), -ethyl-, b.p. 152—153° (*picrate*, m.p. 132—133°), -*n*-, b.p. 169—171° (*picrate*, m.p. 128—129°), and -*iso*-propyl-, b.p. 158—160° (*picrate*, m.p. 166—167°), -*n*-, b.p. 186—187° (*picrate*, m.p. 121.5—122.5°), and -*iso*-butyl-, b.p. 180—181° (*picrate*, m.p. 138—139°), -*n*-, b.p. 205—208° (*picrate*, m.p. 109—110°), and -*iso*-amyl-, b.p. 202—204° (*picrate*, m.p. 145—146°), -amino-*tert*-butyl alcohol. $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\cdot\text{OH}$ gives similarly γ -*n*-, b.p. 216—220° (*picrate*, m.p. 127—128°), and γ -*iso*-butylaminomethyl-*n*-pentan- γ -ol, b.p. 214—216° (*picrate*, m.p. 130.5—131.5°). $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ in aq. NaOH at 30—40° then yields β -*n*-propyl-, m.p. 108—109°, β -*n*-, m.p. 87—88°, and -*iso*-butyl-, m.p. 130—131°, β -*n*-, m.p. 107—109°, and -*iso*-amyl-, m.p. 112—113°, -amino-*tert*-butyl *p*-nitrobenzoate

and γ -*p*-nitrobenzoyloxy- γ -isobutylaminomethyl-*n*-pentane, reduced by Sn-HCl to the corresponding *p*-aminobenzoates, m.p. 123—124° (sulphate, m.p. 138—140° or 150—153°), 116—119° (sulphate, +H₂O), 83.5—84.5° (sulphate, m.p. 142—143°, 158.5—159.5°), 93—95° [sulphate (I), +H₂O, m.p. 163—166°, and anhyd.], an oil (sulphate, m.p. 146—148°), and 122—123° (sulphate, m.p. 131—133°), respectively. The hydrochlorides are oils. The sulphates are too toxic for use by injection, but (I) is a useful surface anæsthetic (rabbit's cornea). R. S. C.

Synthesis of alkamine esters of alkylthiolbenzoic acids. J. J. DONLEAVY and J. ENGLISH, jun. (J. Amer. Chem. Soc., 1940, 62, 220—221).—Interaction of CO₂H·C₆H₄·N₂Cl with K ethylxanthate and Na₂CO₃ (0.5 mol.) at 70° and subsequent treatment with NaOH-R₂SO₄ or -RHal in boiling 70% EtOH gives SR·C₆H₄·CO₂H, which with PCl₅ yields the acid chloride and thence in C₅H₅N (2 mols.) the ester. The following are thus prepared, m.p. in parentheses being those of the hydrochlorides: *m*-methyl-, m.p. 129° (chloride, b.p. 123°/8 mm.), *o*-, m.p. 134° (chloride, b.p. 133°/3 mm.), *m*-, +H₂O, m.p. 98° (chloride, b.p. 127°/3 mm.), and *p*-ethyl-, m.p. 145° (chloride, b.p. 118°/mm.), *o*-, m.p. 121° (chloride, b.p. 145°/3 mm.), and *m-n-propyl*-, m.p. 104° (chloride, b.p. 138°/3 mm.), *o*-, m.p. 98° (chloride, b.p. 151°/3 mm.), and *m-n-butyl*-, m.p. 103° (chloride, b.p. 147°/3 mm.), -thiolbenzoic acid; β -diethylaminoethyl *m-methyl*-, b.p. 185°/5 mm. (153°), *o*-, b.p. 158°/3 mm. (128°), *m*-, b.p. 163°/2 mm. (135°), and *p-ethyl*-, b.p. 160°/3 mm. (166°), *o*-, b.p. 176°/3 mm. (123°), and *m-n-propyl*-, b.p. 172°/2 mm. (110°), *o*-, b.p. 180°/2 mm. (117°), and *m-n-butyl*-, b.p. 200°/4 mm. (110°), -thiolbenzoate; γ -diethylamino-*n-propyl m-methyl*-, b.p. 190°/4 mm. (149°), *o*-, b.p. 184°/3 mm. (121°), *m*-, b.p. 170°/3 mm. (125°), and *p-ethyl*-, b.p. 185°/3 mm. (138°), *o*-, b.p. 182°/3 mm. (87°), and *m-n-propyl*-, b.p. 183°/3 mm. (94°), *o*-, b.p. 193°/2 mm. (96°), and *m-n-butyl*-, b.p. 194°/3 mm. (96°), -thiolbenzoate; β -piperidinoethyl *o*-, b.p. 197°/3 mm. (134°), and *m-ethyl*-, b.p. 173°/3 mm. (139°), *o*-, b.p. 190°/3 mm. (128°), and *m-n-propyl*-, b.p. 182°/3 mm. (116°), *o*-, b.p. 198°/2 mm. (120°), and *m-n-butyl*-, b.p. 198°/3 mm. (114°), -thiolbenzoate; β -dibutylaminoethyl *o-ethyl*-, b.p. 187°/3 mm. (116°), *o-n-propyl*-, b.p. 208°/3 mm. (93°), and *o-n-butyl*-, b.p. 193°/3 mm. (107°), -thiolbenzoate. The esters are local anæsthetics (rabbit's cornea) of low toxicity. R. S. C.

Synthesis of aromatic amino-carboxylic acids. A. I. KIZBER (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 440).—Aromatic amines with Na₂CO₃ or NaHCO₃ at 200° yield, e.g., 2:1-NH₂·C₁₀H₆·CO₂H, 1-aminoanthraquinone-2-carboxylic acid (and the 2:1-isomeride); use of K₂CO₃ or KHCO₃ leads to the formation of other isomerides. F. R. G.

Thujane series. X. Total synthesis of thujone. Synthesis of an isomeride (2-carboxy-2-isopropylcyclopropylacetic acid) of α -thujadicarboxylic acid. P. C. GUHA and M. S. MUTHANNA (J. Indian Inst. Sci., 1939, 22, A, 278—282).—Umbellularie anhydride (cf. A., 1939, II, 66) with a well cooled solution of NaOEt in EtOH affords *Et* 2-carboxy-1-isopropylcyclopropane-1-carboxylate, b.p.

136—138°/5 mm., the acid chloride of which with CH₂N₂ in dry Et₂O gives an oil, decomp. when heated, converted by Ag₂O in warm EtOH followed by dil. aq. Na₂CO₃ into umbellularic acid and 2-carboxy-2-isopropylcyclopropylacetic acid (I), m.p. 80—81°. The m.p. of (I) is depressed by admixture with β -isopropyladipic acid, m.p. 80—81°. J. L. D.

Pinane group. VI. Attempts to synthesise pinonic acid, nopinone, and verbenone. P. C. GUHA and P. L. N. RAO (J. Indian Inst. Sci., 1939, 22, A, 317—325).—*Et trans*-3-carboxy-2:2-dimethylcyclobutylacetate previously described (cf. A., 1938, II, 412) is a mixture containing *trans*-3-carbethoxy-2:2-dimethylcyclobutylacetic acid (I) [amide (II), m.p. 97°]. The chloride of (I) with *p*-NO₂·C₆H₄·NH₂ in C₅H₅N gives the *p-nitroanilide*, m.p. 129—130°, hydrolysis of which [or (II)] gives pinic acid or (I). MgMeI and (I) at 0°/2 hr. and then at the b.p./0.5 hr., followed by esterification, give Et₂ pinate and *Et trans*-2:2-dimethyl-3- α -hydroxyisopropylcyclobutylacetate (III), b.p. 130—135°/5 mm. [corresponding acid (IV) and amide were obtained as gums]. With excess (3.5 mols.) of MgMeI, (III) (80% yield) together with a small amount of *trans*-2:2-dimethyl-1- α -hydroxyisopropyl-3- β -hydroxyisobutylcyclobutane (?) (V), b.p. 110—120°/5 mm., is formed (cf. Grandperrin, A., 1936, 1113). KHSO₄ and (IV) or (III) at 180—200°/1 hr. give a neutral substance, C₂₂H₃₈O₅, b.p. 104—106°/3 mm., 145—147°/14 mm., which absorbs Br and is oxidised by KMnO₄ to H₂C₂O₄ and a gum. Equimol. amounts of *Et cis*-pinonate and MgMeI [as for (I)] afford unchanged material, *cis*-2:2-dimethyl-1- α -hydroxyisopropyl-3-isobutenylcyclobutane (?), b.p. 105—108°/6 mm., probably *cis*-(V), *cis*-(IV), and a lactone, b.p. 121—122°/4 mm. Norpinic semi-aldehyde with CH₂(CO₂H)₂, piperidine, and C₅H₅N at 100°/24 hr. gives a gum, esterification of which yields *Et* β -3-carbethoxy-2:2-dimethylcyclobutylacrylate, b.p. 123—125°/3.5 mm., which yields no cryst. substance when oxidised with KMnO₄ and is reduced (PtO₂-H₂/2.5 atm.) in EtOH to *Et* β -3-carbethoxy-2:2-dimethylcyclobutylpropionate (VI), b.p. 130—132°/4 mm. [corresponding acid (VII), m.p. 55—60°]. The Dieckmann reaction applied to (VI) or pyrolysis of the Pb salt of (VII) gives no nopinone. Norpinyl chloride and ZnMeI (cf. A., 1938, II, 412) afford 1:3-diacetyl-2:2-dimethylcyclobutane, m.p. 104° [disemicarbazone, m.p. 233° (decomp.)], which does not give verbenone with NaOEt. J. L. D.

Thujane series. XI. Synthesis of an isomeride (1-isobutylcyclopropane-1:2-dicarboxylic acid) of α -thujadicarboxylic acid. P. C. GUHA and M. S. NANDE (J. Indian Inst. Sci., 1939, 22, A, 283—285).—*Et* α -bromoishexanoate with CHNa(CO₂Et)₂ in boiling EtOH/7 hr. gives *Et* α -carbethoxy- α' -isobutylsuccinate, b.p. 175—176°/19 mm., which with Br in CCl₄ (first at 70°, then at the b.p.) gives the α -Br-derivative, b.p. 175°/5 mm., converted by boiling NPhEt₃/8 hr. into *Et* α -carbethoxy- α' -isobutylfumarate (I), b.p. 112—115°/2 mm. Prolonged contact of (I) with CH₂N₂ in Et₂O at 0° gives Et₃ 1-isobutylcyclopropane-1:2:2-tricarboxylate, b.p. 108—109°/2 mm., hydrolysed [boiling dil.

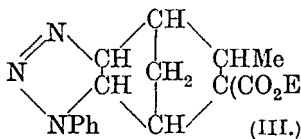
HCl (1:1)/8 hr.] to 1-isobutylcyclopropane-1:2-dicarboxylic acid, m.p. 98—99°. J. L. D.

Addition of aliphatic diazo-compounds to conjugated doubly linked systems. Action of diazomethane and ethyl diazoacetate on cyclopentadiene and cyclohexadienes and their derivatives. P. C. GUHA and G. D. HAZRA (J. Indian Inst. Sci., 1939, 22, A, 263—274).—cyclopentadiene (I), $\Delta^{1:3}$ (II), and 2:3-dimethyl- $\Delta^{1:3}$ -cyclohexadiene (cantharene) (III) do not react with CH_2N_2 (1 mol.) at 0° or room temp. even in presence of MeOH. $\text{CHN}_2 \cdot \text{CO}_2\text{Et}$ (IV) and (I) (1 mol.) at 0°/7 days yield a product which explodes at room temp.; in presence of Cu-bronze, reaction occurs at room temp. to give an unworkable product. (II), (IV), and Cu-bronze at 100° (bath)/6 hr. give *Et* norcarenecarboxylate, b.p. 84°/2.5 mm. [corresponding acid, m.p. 82.5° (anilide, m.p. 195—196°)], reduced (PtO_2 -MeOH- H_2) to *Et* norcanecarboxylate, b.p. 112—114°/19 mm. (corresponding acid, m.p. 97°, the Ba salt of which when heated with ZnO gives norcarane, b.p. 111—112°) (cf. Ebel *et al.*, A., 1929, 312). 1:2-Dimethyl- Δ^1 -cyclohexene with Br- CHCl_3 at 0° gives the dibromide, m.p. 150°, converted by heating with quinoline into (III). (III) and (IV) at 70° in presence of Cu-bronze give *Et* dimethylnorcarenecarboxylate, b.p. 91—95°/2.5 mm., which reacts with Br, decolorises KMnO_4 , and is hydrolysed (5% EtOH-KOH at room temp.) to small amounts of acids, m.p. 140° and 282°, the former sol. and the latter insol. in C_6H_6 . *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2$ with H_2 (3 atm.)/1.5 hr., PtO_2 , and AcOH at room temp. affords Me_2 hexahydroterephthalate, b.p. 132—133°/2 mm., hydrolysed (boiling 8% HCl/6 hr.) to *cis*- (V) and *trans*-hexahydroterephthalic acid. (V) when heated with >2 equivs. of SOCl_2 gives the dichloride, which with Br at 150°/4 hr., followed by MeOH, affords a mixture (A) of Me_2 *cis*-, m.p. 68°, and *trans*-1:4-dibromohexahydroterephthalate, m.p. 150°. 50% EtOH-KOH converts (A) at room temp./48 hr. into 2:3-dihydroterephthalic acid [Me_2 ester (VI), m.p. 85°]. (VI) with CH_2N_2 in Et_2O at 0°/2 days affords Me_2 1:4-endomethylene-1:2:3:4-tetrahydroterephthalate, b.p. 132—134°/3 mm., hydrolysed (boiling 10% HCl/12 hr.) to the acid, m.p. 255°, which is oxidised (3% KMnO_4 at 0°/12 hr.) to cyclopentane-1:1:3:3-tetracarboxylic acid, m.p. 188°. J. L. D.

Aldehydo-acids and aldo-enol-lactones. IV. Specific transformation of certain aldehydo-acids and γ -aldo-enol-lactones in alkali medium. M. M. SCHEMJAKIN (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 768—772).—The truxinic acid (I), m.p. 195—196° (A., 1939, II, 422) (mono-chloride, m.p. 150°, and -anilide, m.p. 241°), is isomerised by conc. HCl at 180—190° to an acid (II), m.p. 245° [chloride, m.p. 144°; MeOH- H_2SO_4 give a *Me* ester (III), m.p. 133°]. (I) and (II) are the two hitherto unknown truxinic acids (structures given). MeOH- H_2SO_4 and (I) give a Me_2 ester, m.p. 183°, isomerised at 260° (1 hr.) to a mixture of (III) and an ester, m.p. 105—107°, hydrolysed to (II) and β -truxinic acid, m.p. 211°, respectively. The Me_2 ester, m.p. 196° (m.p. 198—199°; *loc. cit.*), of (I) is unchanged at 260°.

A. T. P.

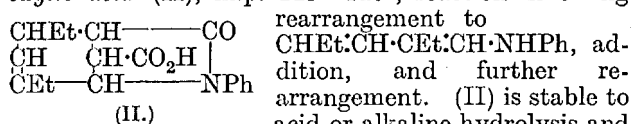
Diene syntheses. XIV. Preparation of allycyclic malonic, cyanoacetic, and acetoacetic esters. K. ALDER and H. F. RICKERT (Ber., 1939, 72, [B], 1983—1992).—Addition of $(\text{CH}_2\text{:CH})_2$ to $\text{CHMe:C}(\text{CO}_2\text{Et})_2$ (I) at 170—180° gives crude *Et*₂ 2-methyl- Δ^4 -cyclohexene-1:1-dicarboxylate, rapidly hydrogenated (PtO_2 in EtOAc) to the saturated ester, which is hydrolysed to 2-methylcyclohexane-1:1-dicarboxylic acid, m.p. 155—156°. Under similar conditions $(\text{CH}_2\text{:CMe})_2$ (II) affords *Et*₂ 3:4:6-trimethyl- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. 147—149°/11 mm., and cyclopentadiene gives *Et*₂ 6-methyl-2:5-endomethylene- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. 138—139°/11 mm., converted by PhN_3 into the hydrotriazole (III), m.p. 158—159°. $\text{CHPh:C}(\text{CO}_2\text{Et})_2$ and (II) at 180° yield *Et*₂



6-phenyl-3:4-dimethyl- Δ^3 -cyclohexene-1:1-dicarboxylate b.p. 156—158°/0.1 mm., m.p. 58°; the acid, m.p. 190°, is decarboxylated at 210° to a mixture of *trans*-, m.p. 157—158°, and *cis*-, m.p. 151°, -6-phenyl-3:4-dimethyl- Δ^3 -tetrahydrobenzoic acid. $\text{CHPr}^t\text{:C}(\text{CO}_2\text{Et})_2$ and (II) at 170—180° give *Et*₂ 3:4-dimethyl-6-isopropyl- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. 155—157°/11 mm., in good yield. At 180° $\text{CHEt:C}(\text{CO}_2\text{Et})_2$ and (II) yield *Et*₂ 3:4-dimethyl-6-ethyl- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. 149—150°/11 mm. *Et*₂ 6-methyl-2:5-endoethylene- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. 155—156°/11 mm., is obtained from (I) and $\Delta^{1:3}$ -cyclohexadiene at 190—200°. $\text{CHMe:C}(\text{CN})\text{:CO}_2\text{Et}$ and (II) at 170—180° give *Et* 1-cyano-3:4:6-trimethyl- Δ^3 -cyclohexene-1-carboxylate, b.p. 146—149°/11 mm., whilst 1:1-dicyano-6-phenyl-3:4-dimethyl- Δ^3 -cyclohexene, b.p. 155—156°/2 mm., m.p. 81—82°, is derived from $\text{CHPh:C}(\text{CN})_2$ and (II) at 185—195°. $\text{CHMe:CAc:CO}_2\text{Et}$ and $(\text{CH}_2\text{:CH})_2$ at 170—180 (12 hr.) give *Et* 1-acetyl-6-methyl- Δ^3 -cyclohexene-1-carboxylate, b.p. 126—128°/11 mm., rapidly hydrogenated in EtOAc to the saturated ester, b.p. 127—129°/11 mm.; (II) at 170—180° affords *Et* 1-acetyl-3:4:6-trimethyl- Δ^3 -cyclohexene-1-carboxylate, b.p. 139—141°/12 mm. *Et* 6-ethoxy-1-acetyl-3:4-dimethyl- Δ^3 -cyclohexene-1-carboxylate, b.p. 153—155°/12 mm. (solidifies when kept), is derived from (II) and $\text{OEt:CH:CAc:CO}_2\text{Et}$ at 170—180°. $[\text{C}(\text{CO}_2\text{Et})_2]_2$ and (II) yield *Et*₄ 4:5-dimethyl- Δ^4 -cyclohexene-1:1:2:2-tetracarboxylate, b.p. 151—153°/0.1 mm., whereas $(\text{CH}_2\text{:CH})_2$ gives *Et*₄ Δ^4 -cyclohexene-1:1:2:2-tetracarboxylate, b.p. 149—151°/0.1 mm. This is readily hydrogenated (PtO_2 in AcOH) to *Et*₄ cyclohexane-1:1:2:2-tetracarboxylate, b.p. 190—192°/11 mm., which is hydrolysed and decarboxylated by alkali to *cis*- and by acid to *trans*-hexahydrophthalic acid. H. W.

Reactions of anils. III. New type of Diels-Alder reaction. H. R. SNYDER, R. B. HASBROUCK, and J. F. RICHARDSON. IV. Reactions of benzylidene- and cinnamylidene-aniline with methyl acetylenedicarboxylate. H. R. SNYDER, H. COHEN, and W. J. TAPP (J. Amer. Chem. Soc., 1939, 61, 3558—3560, 3560—3561).—III. In absence of H_2O , CHPh:CH:CH:NPh and $(\text{:CH:CO})_2\text{O}$ (I) in Et_2O

give <2% of maleanilic acid (cf. Bergmann, A., 1939, II, 36). β -Ethyl- Δ^8 -hexenylideneaniline (prep. from NH_2Ph and the aldehyde at 100°), b.p. $127\text{--}128^\circ/2$ mm., and (I) in dry C_6H_6 give 75–80% of 2-phenyl-5 : 7-diethyl-2-aza[2, 3, 1]dicyclo- Δ^6 -octen-3-one-8-carboxylic acid (II), m.p. $145\text{--}146^\circ$, reaction involving



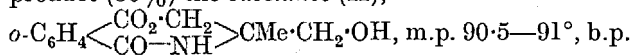
to Na-Hg. With H_2 -PtO₂ in abs. EtOH at 3 atm., it gives the H_2 -derivative, anhyd., m.p. 177° , and $+\text{H}_2\text{O}$, decomp. $120\text{--}130^\circ$, m.p. 177° (amide, m.p. $187\text{--}188^\circ$), also stable to hydrolysis. Vigorous hydrolysis (conc. KOH) of (II) gives, by loss of NH_2Ph and HCO_2H , 3 : 5-diethylbenzoic acid, m.p. 133° , oxidised by $\text{KMnO}_4\text{--K}_2\text{CO}_3$ to $s\text{-C}_6\text{H}_3(\text{CO}_2\text{H})_3$.

IV. $\text{CHPh}\cdot\text{NPh}$ and $(\text{C}\cdot\text{CO}_2\text{Me})_2$ (III) in abs. Et_2O give a small amount of $\text{Me}_2\alpha$ -anilo- α' -benzylidene-succinate, m.p. $192\text{--}193^\circ$, sol. in alkali, formed by addition of NH_2Ph to (III), subsequent isomerisation, and further condensation with PhCHO . Its structure is proved by synthesis from PhCHO and NH_2Ph or $\text{CHPh}\cdot\text{NPh}$ with $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$.

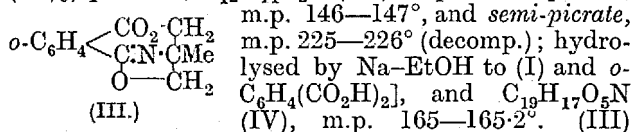
$\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}$ and (III) in petroleum ether give two isomeric substances, $\text{C}_{27}\text{H}_{25}\text{O}_8\text{N}$, m.p. $166\text{--}167^\circ$ and $309\text{--}310^\circ$. R. S. C.

Mechanism of the reaction between phthalic anhydride and an aminodiols. M. M. SPRUNG (J. Amer. Chem. Soc., 1939, 61, 3381–3385).—In accordance with theory, $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ and adipic acid give a thermoplastic, linear-polymeric product, and $\text{NH}_2\cdot\text{CMe}(\text{CH}_2\cdot\text{OH})_2$ (I) with succinic, adipic, malic, or sebacic acid gives cross-linked, insol., infusible resins after 65–75% reaction. However, (I) and $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ or $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ give 100% reaction to a brittle resin without gel-formation; this reaction consists of three stages. At $135\text{--}145^\circ$

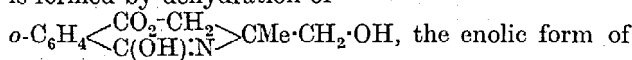
$o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}(\text{CH}_2\cdot\text{OH})_2$ is the main product. Further reaction at $150\text{--}200^\circ$ gives as main product (50%) the substance (II),



Finally, an excess of $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ at $150\text{--}220^\circ$ gives mainly (50%) products, $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$ (III), m.p. $160\cdot5^\circ$ [mono-, m.p. $146\text{--}147^\circ$, and semi-picrate, m.p. $225\text{--}226^\circ$ (decomp.)]; hydro-



is formed by dehydration of



(II), the existence of which is shown by interaction of (II) with >1 mol. of Ac_2O and formation of a Bz_2 derivative, m.p. $121\cdot5^\circ$. The structure of (IV) is unknown; Na-EtOH gives a little $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and a substance, m.p. $227\text{--}228^\circ$ (decomp.). $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ and (II) give a substance (N 3·7%), m.p. $155\text{--}165^\circ$, and a little (III). Small amounts of resinous, linear polymerides are also formed in these condensations. R. S. C.

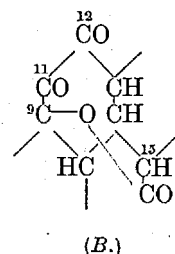
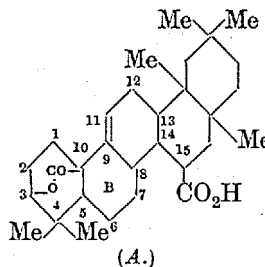
Reaction of 3 : 5-dinitrobenzoic acid with alkali. II. The main product of the reaction, 3 : 3'-dinitroazoxybenzene-5 : 5'-dicarboxylic acid. A. BOLLIGER and F. REUTER (J. Proc. Roy. Soc. New South Wales, 1939, 73, 74–81; cf. A., 1939, II, 478).—3 : 5 : 1-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ in $\sim 0\cdot33\text{N-NaOH}$ is treated with $10\text{--}11\text{N-NaOH}$ for 3–4 hr. at room temp., thus giving 3 : 3'-dinitroazoxybenzene-5 : 5'-dicarboxylic acid (I), m.p. 288° [Me (II), m.p. 137° , and Et₂ (III), m.p. 116° , ester], in 48% yield. Reduction of (I) with $\text{SnCl}_2\text{--conc. HCl}$ or $\text{SnCl}_2\text{--AcOH--HCl}$ gives yellow, amorphous or micro-cryst. products of high m.p. which could not be further purified or identified. Better results are not obtained by use of TiCl_3 , $\text{Na}_2\text{S}_2\text{O}_4$, or $(\text{NH}_4)_2\text{S}$ although in some cases a m-diamine appears to be formed. The Wallach transformation of (I) by the action of hot, conc. H_2SO_4 could be effected only in traces, if at all. (I) can be recryst. from boiling HNO_3 (d 1·4) but the prolonged action of the boiling acid (d 1·48) leads to 3 : 5 : 5'-trinitroazoxybenzene-3'-carboxylic acid (IV), m.p. 216° (NH_4 salt), which forms colourless to dark red solutions in alkali hydroxide according to the concn. used. (I), (II), (III), and (IV) with COMe_2 and other Me ketones in the Janowski reaction give colours similar to those obtained with $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ and 3 : 5 : 1-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$. 3 : 3'-Dinitro- and 2-nitro-azoxybenzene also give positive results whereas with azoxybenzene, azoxyanisole, azoxybenzene-4'-carboxylic and -3 : 3'-dicarboxylic acid the results are negative. In azoxy-compounds the presence of at least 1 NO_2 is conditional for this colour reaction. H. W.

Preparation of mellitic acid.—See B., 1940, 114.

Compounds of the ætiocholanolic acid series.—See B., 1940, 172.

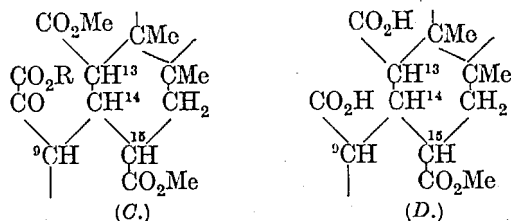
Isomerides of 3 : 5 : 6-trihydroxycholanolic acid. J. HATTORI (J. Pharm. Soc. Japan, 1939, 59, 131–132).—"β- and γ-Trihydroxycholanolic acid" (A., 1939, II, 425) are 3 : 6-dihydroxy-5-methoxy- and 3 : 5-dihydroxy-6-methoxy-cholanolic acid, respectively. The prefix should be omitted in the α-series. The same changes apply to derivatives of the acids. R. S. C.

Quinovic acid. VIII. W. SCHMITT and H. WIELAND (Annalen, 1939, 542, 258–273; cf. A., 1939, II, 425).—Structure (A) is now assigned to novic



acid; the isomeric hydroxyketo-acids, $\text{C}_{30}\text{H}_{42}\text{O}_6$ (A., 1936, 849), derived by oxidation have $\text{C}_{(9)}\cdot\text{OH}$ and $\text{C}_{(11)}\cdot\text{O}$ and differ in the steric arrangement at $\text{C}_{(9)}$. Novaquinone (I) [monoisimine, m.p. 217° , from (I) and 2N-NH_3 in EtOH] is considered to be (B). Oxidation of (I) with stabilised H_2O_2 in EtOH-KOH results in fission between $\text{C}_{(11)}$ and $\text{C}_{(12)}$ to give the dilactonic

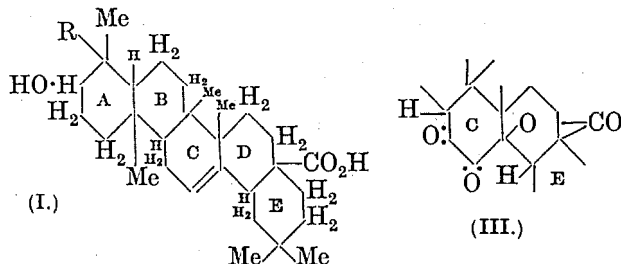
dicarboxylic acid, $C_{30}H_{42}O_8$ (II) (*loc. cit.*) [*anhydride*, m.p. 260° (decomp.)]; use of pure H_2O_2 in EtOH-KOH results in ~50% each of (II) and dihydronovaquinone (III) whilst H_2O_2 -dioxan at 100° affords (III) only. Short treatment of the Me_2 ester of (II) with warm *N*-MeOH-KOH causes fission of the $C_{(9)}-C_{(15)}$ lactone group; the resulting product with $Et_3O-CH_2N_2$ gives a Me_3 ester, $C_{33}H_{50}O_9$ (IV), m.p. 180° (falls when kept in air and light), which does not contain OH (Zerevitinov). (IV) (or its intermediate) has undergone ring-chain tautomerism with fission of ring B between $C_{(9)}$ and $C_{(10)}$ to a CO-derivative; (IV) thus becomes (C, R = Me). Hydrolysis (*N*-MeOH-KOH) of (IV) yields the Me_2H ester (C, R = H), m.p. 183° , which with conc. H_2SO_4 in CO_2 at 35° gives CO and the trans- $Me H_2$ ester (V) (as D), $C_{30}H_{46}O_8$,



decomp. $240-250^\circ$ according to rate of heating (the Me_3 ester has m.p. 179°). The *anhydride*, m.p. 185° , from (V) at 250° , is hydrolysed (MeOH-KOH) to and also obtained from the cis- $Me H_2$ ester (as D), m.p. $190-200^\circ$ (decomp.), whence the Me_3 ester, m.p. 186° . Reduction (Zn dust, AcOH) of (IV) affords a compound, ? $C_{33}H_{52}O_8$, m.p. 238° [no colour with $C(NO_2)_4$ or conc. H_2SO_4], which may be as C with $CO = CH_2$. The structures of some of the yellow oxidation products (A., 1932, 954) of quinovic acid are discussed.

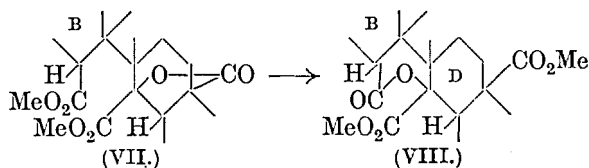
Treatment of (III) with $Et_2O-CH_2N_2$ causes rearrangement [$\cdot C(OH) \cdot C(OH) \cdot \rightarrow \cdot CO \cdot CH(OH) \cdot$] to the α -ketol, $C_{30}H_{42}O_6$, m.p. 242° (decomp.), oxidised (CrO_3 -AcOH at 100°) to (I). Me_2SO_4 and (III) in 4*N*-NaOH at 50° give a compound, $C_{30}H_{41}O_5 \cdot OMe$, m.p. 192° . H. B.

Constitution of acid saponinins. XV. Hederagenin and oleanolic acid. Z. KITASATO [with M. SINKAI] (*Acta Phytochim.*, 1939, **11**, 1-25; cf. A., 1937, II, 462; 1939, II, 30).—Oleanolic acid and hederagenin are now considered to be (I) with R = Me and $CH_2 \cdot OH$, respectively (cf. also Ruzicka *et al.*, A., 1938, II, 447; 1939, II, 29; Haworth, *Ann. Repts.*, 1937, **34**, 338). Oleanintrinsicarboxylic acid (II) and CrO_3 -AcOH, followed by CH_2N_2 , give the *monolactone*,



m.p. 227° , of Me_2 keto-oleanintrinsicarboxylate. The Me_3 ester of (II) is oxidised to Me_3 keto-oleanintri-

carboxylate, m.p. 182° . Me ketodihydroacetyloleanolate (cf. Ruzicka *et al.*, A., 1937, II, 382) or hydroxyacetyloleanolactone, or Me acetyloleanolate, and $CrO_3-H_2SO_4$ -AcOH give the *diketo-oleanolactone* (III), m.p. 286° . Me ketoacetyloleanolate is oxidised to the *hydroxydiketo-oleanolactone*, $C_{32}H_{46}O_7$, m.p. 286° (decomp.) (cf. Ruzicka *et al.*, A., 1939, II, 220). The Me ester of ketodiacetylhederagenin and $CrO_3-H_2SO_4$ -AcOH give a *hydroxydiketolactone*, $C_{34}H_{48}O_9$, m.p. 274° . The Me ester of diacetylhederagenin is oxidised to a *diketo-acid*, $C_{30}H_{46}O_7$, m.p. 257° [Me ester, $+0.5H_2O$, m.p. 210° (*diacetate*, m.p. $229-230^\circ$)], and (after acetylation) a *substance*, $C_{34}H_{48}O_8$, m.p. 285° . Me dehydroacetyloleanolate (A., 1936, 1261) similarly gives a hydroxytricarboxylic acid (Me ester, $C_{34}H_{50}O_9$, m.p. 256°) (formula given). Ketoacetyloleanolactone (A., 1936, 1261) and Br-AcOH give the *bromolactone*, $C_{32}H_{47}O_5Br$, m.p. $>300^\circ$ (cf. A., 1932, 1035), converted by Zn-AcOH into ketodihydroacetyloleanolic acid, m.p. $>300^\circ$, or by KOH-MeOH into a neutral *substance*, $C_{30}H_{46}O_5$, m.p. 265° (Ac derivative, m.p. 232°). Ketoacetyloleanolic acid (IV) and Br-AcOH give a *bromolactone*, $C_{32}H_{47}O_4Br$, m.p. $240-245^\circ$ (decomp.), reduced by Zn-AcOH to a mixture of (IV) and a *keto-acid* [Me ester, $C_{32}H_{52}O_5$, m.p. 250° (decomp.), m.p. 272° , $[\alpha]_D^{25} -39.0^\circ$ in $CHCl_3$]. ψ -Ketoacetyloleanolic acid (V) (cf. A., 1934, 1223) gives a *bromolactone*, $C_{32}H_{45}O_5Br$, m.p. $256-257^\circ$ (decomp.), converted by Zn-AcOH into (V) or by KOH-MeOH into ψ -keto-oleanolic acid. ψ -Ketohederagenin (VI) gives a *bromolactone*, $C_{30}H_{45}O_5Br$, m.p. 247° (decomp.), converted by Zn-AcOH into (VI). The monolactone (VII) of Me_4 oleanolpentacarboxylate is converted by 5% KOH-MeOH into the iso-form (VIII), m.p. $198-200^\circ$. Thermal decomp. of oleanintrinsicarboxylic acid (*loc. cit.*)

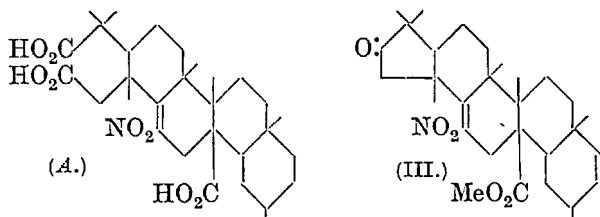


is considered to involve loss of the CO_2H between rings D and E and production of a double linking in ring D.

Absorption spectra of diketodehydro- and ψ -keto-diacetylhederagenin esters are examined. A. T. P.

Saponins. XIV. Oxidation of oleanonic acid with nitric acid. S. KUWADA and K. TAKEDA (*J. Pharm. Soc. Japan*, 1939, **59**, 121-124).—Oleanonic acid, m.p. 166° (decomp.), $[\alpha]_D^{15} +102.6^\circ$ in $CHCl_3$ (*oxime*, decomp. 290° ; *semicarbazone*, decomp. 271° ; Me ester, m.p. $184-185^\circ$), is converted by fuming HNO_3 and AcOH into *nitro-oleanoltricarboxylic acid* (I) (A), decomp. 244° , $[\alpha]_D^{15} +130.8^\circ$ in abs. EtOH [*anhydride*, decomp. 230° ; Me_3 ester (II), decomp. 178° , $[\alpha]_D^{15} +90.3^\circ$ in $CHCl_3$]. (I) is unchanged by boiling 10% KOH-MeOH whereas (II) is transformed by a Dieckmann reaction into the Me ester (III), decomp. $234-235^\circ$, $[\alpha]_D^{15} +193.7^\circ$ in $CHCl_3$ (*oxime*, m.p. 150°). Fuming HNO_3 and AcOH transform (III) into *nitro-oleanintrinsicarboxylic acid* (A, with CO_2H for $\cdot CH_2 \cdot CO_2H$),

decomp. 225—226°, the Me_3 ester, decomp. 206—207°, $[\alpha]_D^{25} +105.8^\circ$ in $CHCl_3$, of which is not converted by



boiling 10% KOH-MeOH into a ketonic substance. M.p. are corr. H. W.

Formation of amino-aldimine complexes by hydrogenation of amino-nitriles in presence of nickel. M. DELÉPINE and K. A. JENSEN (Bull. Soc. chim., 1939, [v], 6, 1663—1670; cf. A., 1938, II, 247).—4-Amino-5-cyano-2-ethylpyrimidine and H_2 (Raney Ni + $NiCl_2$ in aq. NH_3 -EtOH) give [after hydrolysis (aq. $AcOH$)] the corresponding 5-aldehyde (I), m.p. 164° [oxime, volatilises without melting; 2:4-dinitrophenylhydrazone, m.p. 290° (decomp.)], and 5-aminomethyl derivative [dipicrate, m.p. 240° (decomp.)], and a complex (II), $(C_7H_9N_4)_2Ni \cdot 4H_2O$. (I) and Ni-aq. NH_3 -EtOH give (II). A similar hydrogenation of $o-NH_2 \cdot C_6H_4 \cdot CN$ gives $o-NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$, a complex, $C_{14}H_{14}N_4Ni$ (as isolated by Pfeiffer *et al.*, A., 1938, II, 62), and a complex imine; both complexes are obtained from $o-NH_2 \cdot C_6H_4 \cdot CHO$. Hydrogenation of $o-OH \cdot C_6H_4 \cdot CN$ (in MeOH) or $o-OH \cdot C_6H_4 \cdot CHO$ gives a similar complex. Structural formulæ of complexes are discussed.

A. T. P.

Colour of dyes.—See A., 1940, I, 56.

Reactions of anils. II. Addition of methyl ketones to benzyldeneaniline in presence of boron fluoride. H. R. SNYDER, H. A. KORNBERG, and J. R. ROMIG (J. Amer. Chem. Soc., 1939, 61, 3556—3558; cf. A., 1938, II, 444).— $CHPh \cdot NPh$ and BF_3 give a 1:1 co-ordination compound, m.p. 135—145°, which with $COMeR$ readily gives β -anilino- β -phenylethyl Me (I), m.p. 88—89°, Et, m.p. 120—121°, Bu^t , m.p. 80—81°, n-amyl, m.p. 78—79°, β -phenylethyl, m.p. 98—99.5°, Bu^i (II), m.p. 148—149°, and β -methyl-n-butyl ketone, m.p. 72—73°, Ph β -anilino- β -phenylethyl ketone, m.p. 166—167° (lit. 173°), and 2- β -anilino- β -phenylethylcyclopentanone, m.p. 163—164°. $CH_2(CO_2Et)_2$ gives a little of an additive compound, m.p. 98—99°. Numerous other compounds do not react with the complex or give oils. The condensation is not reversible, as (I) and (II) are stable in $COMeBu^i$ and $COMe_2$, respectively. (I) is not obtained from $CHPh \cdot CH \cdot COMe$ and NH_2Ph .

R. S. C.

Rates of reaction of cyclopropyl ketimines with water. J. B. CLOKE (J. Amer. Chem. Soc., 1940, 62, 117—119; cf. A., 1929, 703).—cycloPropyl Et ketimine hydrochloride (I) (prepared from cyclopropyl cyanide by interaction successively with $MgEtBr$, liquid NH_3 , and HCl in Et_2O in absence of H_2O), m.p. 95—97° (shrinks 70—80°) (98.5—100.5°; bath preheated to 87°), is hydrolysed more readily than is $C_3H_5 \cdot CPh \cdot NH \cdot HCl$ (both hydrolyses are retarded by HCl), but less readily than is the free base. Thus, (I)

probably exists largely as $CHMe \cdot C(C_3H_5) \cdot NH_2 \cdot HCl$ in aq. solution. Measurement of the rates of hydrolysis is described in detail. R. S. C.

Thujane series. IX. Synthesis of umbellulonic acid. P. C. GUHA and M. S. MUTHANNA (J. Indian Inst. Sci., 1939, 22, A, 275—277; cf. Tutin, J.C.S., 1906, 89, 1113).—Umbellularic anhydride (cf. Rydon, A., 1936, 993) with $MgMeI$ in boiling $C_6H_6/1$ hr. affords umbellulonic acid, b.p. 190—191°/50 mm. [oxime, m.p. 145—146°; semicarbazone, m.p. 169—170° (cf. A., 1938, II, 336)], oxidised ($NaOBr$) to umbellularic acid. J. L. D.

Keten in the Friedel-Crafts reaction. I. Direct acetylation of aromatic hydrocarbons with keten. J. W. WILLIAMS and J. M. OSBORN (J. Amer. Chem. Soc., 1939, 61, 3438—3439).—Gradual addition of $AlCl_3$ (1.5 mols.) to pure keten (excess) and C_6H_6 (1.1 mols.) in CS_2 at 0° gives 32.7% of $COPhMe$. Similarly are obtained α - $C_{10}H_7 \cdot COMe$ (34.8%) (2:4-dinitrophenylhydrazone, m.p. 259°), β -tetrahydronaphthyl Me ketone (19.6%) (2:4-dinitrophenylhydrazone, m.p. 236°), and (at 30°) p - $C_6H_4Ph \cdot COMe$ (23.4%). R. S. C.

Relative oxidation potentials of ketones. F. W. COX and H. ADKINS (J. Amer. Chem. Soc., 1939, 61, 3364—3370).— $CORR'$ and $CHR'R''OH$, in which one radical is aryl, are equilibrated by $Al(OBu^i)_3$ in PhMe at 100° and the amounts of aromatic ketone determined polarographically. Reaction in each direction gives the same result usually after 150—200 hr., but this does not represent equilibrium because of a side-reaction, $3CHR_2 \cdot OH + Al(OBu^i)_3 \rightarrow 3COR_2 + 3C_4H_{10} + Al(OH)_3$, which at 100° leads in 132 hr. to the following yields of ketone: $COPh_2$ 4, $COPhEt$ 5.5, $COPhPr^a$ 1, $COPhPr^s$ 2.4, $COPhBu^a$ 1.2, and $COPh \cdot C_5H_{11-n}$ 4.3%. True equilibrium is obtained by starting with approx. equilibrated amounts of both ketones and both alcohols and allowing reaction to proceed for a shorter time. $COPh_2$ is usually taken as one component, but, with one exception, results are concordant also with other ketones. The oxidising power (relative vals. given) of the following ketones increases in the order quoted: $COPr^s$, $COBu^i$, $COPr^a$, $COBu^s$, $COEt_2$, $COPhBu^i$, $COPhPr^a$, $COPhBu^a$, $COPh \cdot C_5H_{11-n}$, $COPhEt$, $COPhPr^s$, $COPh_2$, and cyclohexanone. Vals. for $COBu^s$ are uncertain owing to its slow reaction and for cyclohexanone owing to self-condensation.

R. S. C.

Nitrones. V. Certain acyldiphenylmethanes and the dyes therefrom. F. KRÖHNKE (Ber., 1939, 72, [B], 1731—1735).—Benzoyltetramethyldiaminodiphenylmethane (I), m.p. 168°, is obtained from $CHBz(OH)_2$ and $NPhMe_2$ in AcOH at 100°, from phenacylpyridinium bromide, PhNO, and $NPhMe_2$ in EtOH at 20°, or, as hydrobromide, m.p. 227—228° (decomp.), from benzoyl-N-phenylnitron, C_5H_5N , HBr, and $NPhMe_2$ at 20°. (I) is oxidised by PbO_2 and HCl at 2° to the dye, isolated as the zincchloride and the perchlorate, which when basified with NH_3 affords the carbinol base, $C_{24}H_{26}O_2N_2$, m.p. 153—154°. (I) gives an oxime, m.p. 160° (softens at 158°), which is oxidised by PbO_2 to a blue dye but does not appear to yield a phenylhydrazone. MeI in MeOH

converts (I) at 100° into the *dimethiodide*, transformed by NaClO₄ into the *diperchlorate*, m.p. 281° (decomp.). The following *-tetramethylldiaminodiphenylmethanes* are described: *p-toluoyl-*, m.p. 125° (*hydrobromide*, m.p. 228—229°); *2-naphthoyl-*; *p-chlorobenzoyl-*, m.p. 148°; *trimethylacetyl-*, m.p. 158—159°. *Acetyltetramethylldiaminodiphenylthiophen* has m.p. 168—169°. H. W.

Condensations brought about by bases. VIII. Conversion of ethyl α -benzoylisobutyrate into ethyl benzoate and *isobutyrylisobutyrate* in presence of sodium ethoxide and triphenylmethane. Reversibility of the Claisen type of condensation. C. R. HAUSER and B. E. HUDSON, jun. (J. Amer. Chem. Soc., 1940, 62, 62—66).—CMe₂Bz·CO₂Et is converted by NaOEt and CHPh₃ (not in absence of CHPh₃) in Et₂O at room temp. (5 days) into EtOBz and Pr^{*β*}CO·CMe₂·CO₂Et (cf. A., 1938, II, 143), the latter product being present in the enolic form since treating the crude product with Pr^{*β*}COCl gives 32% of Pr^{*β*}CO·CMe₂·CO·CMe₂·CO₂Et. NaOEt in dry Et₂O converts CMe₂Ac·CO₂Et into Pr^{*β*}CO₂Et, CH₂Ac·CO·CMe₂·CO₂Et, and EtOAc. The reactions are explained on the basis of the reversibility of the Claisen condensation. R. S. C.

Friedel-Crafts syntheses with tricarballyl chloride and α -phenyltricarballyl chloride. W. BORSCHKE and H. SCHMIDT (Ber., 1939, 72, [B], 1827—1833).—Tricarballic acid is readily obtained by hydrogenation (Pd-C in H₂O) of aconitic acid if pure materials are used. Tricarballyl chloride (I), C₆H₆, and AlCl₃ afford α -phenacyl- $\gamma\gamma$ -diphenyl- γ -butyrolactone (II), m.p. 137—138° (oxime, m.p. 203—205°; 2:4-dinitrophenylhydrazone, m.p. 219—221°; Br-derivative, ? CHBrBz·CH< $\frac{\text{CH}_2\text{CPh}_2}{\text{CO-O}}$, m.p. 141—142°), and β -phenacyl- $\gamma\gamma$ -diphenyl- γ -butyrolactone, m.p. 108—110° (2:4-dinitrophenylhydrazone, m.p. 159—161°). The structure of (II) follows from its ready conversion into 3-keto-6-phenyl-4- β -hydroxy- $\beta\beta$ -diphenylethyl-2:3:4:5-tetrahydropyridazine, m.p. 195—196°. Reaction between (I) and PhMe is more complex and appears to be governed by uncontrollable factors. Under apparently identical conditions the following substances have been isolated in different experiments: α -tolacyl- $\gamma\gamma$ -ditolyl- γ -butyrolactone, m.p. 133—134° (2:4-dinitrophenylhydrazone, m.p. 187—189°), converted by N₂H₄·H₂O in boiling EtOH into 3-keto-6-tolyl-4- β -hydroxy- $\beta\beta$ -ditolylethyl-2:3:4:5-tetrahydropyridazine, m.p. 201—202°; dimethylanthracene, m.p. ~220°; (?) β -tolacyl- $\gamma\gamma$ -ditolyl- γ -butyrolactone 2:4-dinitrophenylhydrazone, m.p. 165—167°; ditolylacetic acid, m.p. 163—166°, isolated as its 2:4-dinitrophenylhydrazone, m.p. 208—210°; $\gamma\gamma$ -ditolyl- γ -butyrolactone- α -, m.p. 190—192°, and - β -, m.p. 116—117°, *acetic acid*. The sole cryst. product from (I) and *m*-xylene is a substance, C₃₀H₃₂O₃, m.p. 174—176°, probably xylacyldixylylbutyrolactone; it does not appear to react with 2:4-(NO₂)₂C₆H₃·NH·NH₂. Et₃ α -phenyltricarballylate, b.p. 212°/12 mm., is conveniently obtained from Et₂ maleate and CH₂Ph·CO₂Et. α -Phenyltricarballyl chloride, AlCl₃, and C₆H₆ yield a lactonic acid, C₂₄H₂₀O₄, m.p. 230—233°, which does not give a 2:4-dinitrophenylhydrazone. H. W.

F (A., II.)

Addition of methoxyamine to $\alpha\beta$ -unsaturated ketones. Rearrangement [of the products] to β -methoxyamino-ketones. A. H. BLATT (J. Amer. Chem. Soc., 1939, 61, 3494—3499).—NH₂·OMe (“methoxyamine”) gives oxime Me ethers of aldehydes or reactive ketones, but the hydrochloride reacts similarly with any CO-compound. NH₂·OMe adds to CHAr·CH·COAr (A) in hot or cold EtOH by 1:4 addition to give good yields of OMe·NH·CHAr·CH₂·COAr (B) and often OMe·N(CHAr·CH₂·COAr)₂ (C). This addition is reversed by distilling (B) (except at 1 mm.) or by heating (B) with PhCHO in EtOH [gives CHPh·N·OMe and (A)]. Ac derivatives of (B), prepared by cold or warm Ac₂O, regenerate (A) when heated alone or treated with cold NaOMe·MeOH. Salts of (B) are readily hydrolysed by cold H₂O, but in EtOH give (A) and its oxime Me ether. Structures are proved by oxidation of the hydrochloride of (B) (Ar = Ph) by HOCl to *dibenzoylmethanemono-oxime Me ether*, m.p. 114—115°, obtained also with some *dioxime Me₂ ether*, m.p. 57·5—58·5°, from CH₂Bz₂ by NH₂·OMe·HCl in EtOH and by addition of NH₂·OMe to CPh₂·COPh in MeOH (the primary product, OMe·NH·CPh₂·CH·COPh, rearranges spontaneously). With 2N-NaOMe at ~60° (later room temp.), (B) loses MeOH and rearranges to CHAr·C(NH₂)·COAr (D), readily hydrolysed to α -diketones. The following are described. β -Methoxyamino- β -phenylpropiophenone, m.p. 54—55° (Ac derivative, m.p. 95·4—95·5°; hydrochloride, m.p. 133—134°). β -Methoxyamino- β -phenyl-*p*-methylpropiophenone, m.p. 43—44° (Ac derivative, m.p. 118—119°). *p*-Chloro-, m.p. 51—52° (Ac derivative, m.p. 142—143°), *p*-methoxy-, m.p. 52—53° (Ac derivative, m.p. 115—116°), and *p*-bromo- β -methoxyamino- β -phenylpropiophenone, m.p. 66—67° (Ac derivative, m.p. 157—158°). β -Methoxyamino- β -*p*′-chloro-, m.p. 67—68° (Ac derivative, m.p. 91—92°), and - β -*p*′-bromo-phenylpropiophenone, m.p. 52—53° (Ac derivative, m.p. 91—92°). β -Acetmethoxyamido- β -*p*-anisylpropiophenone, m.p. 130—131°. *N*-Methoxydi-(γ -keto- $\alpha\gamma$ -diphenyl-, m.p. 178—179°, - γ -phenyl- α -*p*-tolyl-, m.p. 185—186°, and - α -phenyl- γ -*p*-anisyl-, m.p. 183—184°, -propyl)amine. Ph (D; Ar = Ph), m.p. 100—101°, *p*-tolyl, m.p. 92—93°, and *p*-chloro-, m.p. 81—82°, and *p*-bromo-phenyl α -aminostyryl ketone, m.p. 103—104°. Ph *p*′-chloro-, m.p. 88—89°, and *p*′-bromo- α -aminostyryl ketone, m.p. 114—115°.

R. S. C.

Use of hydrogen fluoride in acylations and cyclisations. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1940, 62, 49—53).—Except in the case of acenaphthene (I) (A., 1939, II, 325), HF offers few advantages for acylation of aromatic hydrocarbons. 3-Acetoperinaphthene, b.p. 170—175°/2 mm. (nomenclature: A., 1939, II, 356) [unstable picrate: C₆H₃(NO₂)₃ compound, m.p. 114—114·5°], is obtained in 71% yield from perinaphthene, Ac₂O or AcOH, and HF in a little Et₂O. Its structure is proved by oxidation by Na₂Cr₂O₇ in AcOH at 75—90° to 4:1:8-C₁₀H₅Ac(CO)₂O, m.p. 193—195° (lit. 189°, 191—192°), and by KOCl to 3-perinaphthoic acid, m.p. 188·4—189°. Hydrindene and HF with AcOH give 73% of 5-aceto- (oxidised to hydrindene-5-carboxylic acid, new m.p. 179·5—181·5°), with BzCl

(1 mol.) give 75% of 5-benzoyl-, and with α - $C_{10}H_7\cdot CO_2H$ give 90% of 5- α -naphthoyl-hydrindene, m.p. 71—72° (pyrolysis gives tars). At 100°/4 atm. in a steel vessel, (I), Ac_2O , and HF give 37% of 1-acetoacenaphthene. 1-Acenaphthoyl chloride is converted by H_2 -2% Pd-BaSO₄ and a little quinoline-S in xylene at 150—160° into 1-acenaphthaldehyde (72%), m.p. 99.5—100.5° (purified as NaHSO₃ compound). β - $C_{10}H_7\cdot CHO$ is similarly prepared in 84% yield. Reaction at > room temp. effects also other condensations. Thus, at 50—60° $C_{10}H_8$, Ac_2O , and HF give 1- and 2- $C_{10}H_7\cdot COMe$, containing more than usual of the 2-compound, and phenanthrene (II) at 50—55° gives 3- and some 2-acetophenanthrene. Heating (II), $CHMe\cdot CH\cdot CO_2H$, and HF at 3 atm. gives mixed ketomethylcyclopentanophenanthrenes, b.p. 215—225°/2 mm. o - β - $C_{10}H_7\cdot CO\cdot C_6H_4\cdot CO_2H$, m.p. (+0.5 C_6H_6) 129—131° and then ("anhyd.") 166—167° (lit. 168°), Zn dust and a trace of $CuSO_4$ in boiling, aq. NaOH give o - β - $C_{10}H_7\cdot CH_2\cdot C_6H_4\cdot CO_2H$, m.p. 134—136° or, after resolidification, 139.5—140° (lit. 136—137°), which with HF followed by $MgMeCl$ at room temp. affords 14% of 9-methyl- or with HF and then $CH_2\cdot CH\cdot CH_2\cdot MgBr$ gives 35% of 9-allyl-1:2-benzanthracene, m.p. 115—116°. 1:7- $C_{10}H_6MeBr$ [isolated as $C_6H_3(NO_2)_3$ compound, m.p. 92.5—93°] gives 8:2- $C_{10}H_6Me\cdot CO\cdot C_6H_4\cdot CO_2H$ - o (76%) and thence 8:2- $C_{10}H_6Me\cdot CH_2\cdot C_6H_4\cdot CO_2H$ (60%) (cf. A., 1938, II, 91), which with HF at room temp. gives 1'-methyl-2:3-benz-10-anthrone (III), m.p. 175—176° (slow heating) or 171° (immediate), oxidised by CrO_3 -AcOH to 1'-methyl-2:3-benzanthraquinone, m.p. 227—229°, resistant to $Na_2S_2O_4$. An excess of $MgMeCl$ converts (III) into 10:1'-dimethyl-2:3-benzanthracene [1:6-dimethylnaphthacene], dimorphic, m.p. 138—139° and (unstable) 133° [isolated by chromatography; picrate, m.p. 164—165°; $C_6H_3(NO_2)_3$ compound, m.p. 166.5—167.5°], the structure of which is confirmed by its absorption spectrum [BOWEN]. M.p. are corr. R. S. C.

Sulochrin, a mycelial constituent of *Oospora sulphurea-ochracea*. H. NISHIKAWA (Acta Phytochim., 1939, 11, 167—185; cf. A., 1937, III, 99).—Mycelium extracts afford sulochrin (I), m.p. 262°, almost certainly *Me* 2:6:4'-trihydroxy-6'-methoxy-4-methylbenzophenone-2'-carboxylate (triacetate, m.p. 164°), converted by short treatment with cone. H_2SO_4 at room temp. into *p*-orsellinic acid, m.p. 176° (decomp.), and *Me* 3-hydroxy-5-methoxybenzoate, new m.p. 97° (KOH-MeOH gives the acid, m.p. 203°). The latter and KOH + a little H_2O at >200° give 3:5:1-(OH)₂ $C_6H_3\cdot CO_2H$. (I) and CH_2N_2 - $COMe_2$ - Et_2O give *Me* 6-hydroxy-2:4':6'-trimethoxy-4-methylbenzophenone-2'-carboxylate (dimethylsulochrin) (II), m.p. 158° (acetate, m.p. 157°), converted by H_2SO_4 into 3-hydroxy-5-methoxy-*p*-toluic acid, new m.p. 176°, and 3:5:1-(OMe)₂ $C_6H_3\cdot CO_2Me$. (I) and KOH + a little H_2O at ~250° give 2:6:4':6'-tetrahydroxy-4-methylbenzophenone-2'-carboxylic acid (anhyd., + H_2O , and + $1Et_2O$), darkens and decomp. ~285—290°, methylated (CH_2N_2) to (II). Boiling 10% or 1% KOH-MeOH converts (I) into 3:8-dihydroxy-6-methyl-xanthone-1-carboxylic acid, m.p. 295° (decomp.) (cf. A., 1936, 1247) [diacetate, m.p. 207° (*Me* ester, m.p.

124°)], or its *Me* ester, m.p. 266° (also from the acid), respectively, both converted by CH_2N_2 in Et_2O - $EtOH$ into *Me* 8-hydroxy-3-methoxy-6-methylxanthone-1-carboxylate, m.p. 188° (acetate, m.p. 207°; free acid, m.p. 262°), converted by prolonged treatment with $COMe_2$ - Et_2O - CH_2N_2 into (III) (below). Boiling 0.5% KOH-MeOH and (II) give *Me* 3:8-dimethoxy-6-methylxanthone-1-carboxylate (III), m.p. ~250° [free acid (IV), m.p. 272°], and 6-hydroxy-2:4':6'-trimethoxy-4-methylbenzophenone-2'-carboxylic acid (V), m.p. 230°. (II) and 10% aq.- or MeOH-KOH give (IV) or (IV) + (V), respectively. A. T. P.

Preparation of substituted cyclopentanones. II. H. A. WEIDLICH and M. MEYER-DELIUS (Ber., 1939, 72, [B], 1941—1949; cf. A., 1939, II, 480).—Gradual addition of Br in CCl_4 to well-cooled 2:6- $C_{10}H_6Ac\cdot OMe$ in CCl_4 causes the separation of an orange-coloured additive product, transformed by $NaHCO_3$ in $CHCl_3$ into 5-bromo-6-methoxy-2-bromoacetylnaphthalene (I), m.p. 132—135°, which yields 5-bromo-6-methoxy-2-naphthacetylpyridinium bromide, decomp. 243°; the best results are obtained with a 25% excess of Br. Brominations under varied conditions in $CHCl_3$ from which additive compounds do not separate give 5-bromo-, m.p. 126°, and 5:7-dibromo-, m.p. 143—146°, -6-methoxy-2-acetylnaphthalene (which contain Br in the nucleus since they do not react with C_5H_5N), and 5-bromo-6-methoxy-2-dibromoacetylnaphthalene, m.p. 164—165°, converted by protracted heating with C_5H_5N into methylenedipyridinium bromide, m.p. 255—258°. Gradual addition of (I) to $COEt\cdot CHNa\cdot CO_2Et$ in Et_2O gives *Et* γ -keto- α -propionyl- γ -5-bromo-6-methoxy-2-naphthylbutyrate (II), m.p. 100—101°, with a compound, $C_{46(45)}H_{39(37)}O_9Br_2$, m.p. 208—210°; in one instance *Et* β -keto- α -di-5-bromo-6-methoxy-2-naphthacylvalerate, m.p. 187—188°, was isolated. (II) is transformed by boiling 2% NaOH into 3-5'-bromo-6'-methoxy-2'-naphthyl-2-methyl- Δ^2 -cyclopentenone (III), m.p. 175—177°, occasionally accompanied by 3-hydroxy-3-5'-bromo-6'-methoxy-2'-naphthyl-2-methylcyclopentanone, m.p. 150—151°; if the alkaline treatment is insufficiently prolonged the product contains unchanged ester which passes during distillation into *Et* 5-5'-bromo-6'-methoxy-2'-naphthyl-2-ethylfuran-3-carboxylate, m.p. 108—110° (acid, m.p. 249°). Hydrogenation (PdO on $CaCO_3$ in $EtOH$ containing KOH) of (III) rapidly gives 3-6'-methoxy-2'-naphthyl-2-methyl- Δ^2 -cyclopentenone (IV), m.p. 113—116° [semicarbazone, m.p. 269° (decomp.)], which with more H_2 gives also trans-3-6'-methoxy-2'-naphthyl-2-methylcyclopentanone (V), m.p. 81—83° [semicarbazone, m.p. 236—237° (decomp.)]. In $EtOH$ - $EtOAc$ containing PdO, (III) absorbs 2 H_2 with production of a little initial material, cis-3-6'-methoxy-2'-naphthyl-2-methylcyclopentanone (VI), m.p. 119—121° [semicarbazone, m.p. 239—240° (decomp.)], and cis-3-6'-methoxy-2'-naphthyl-2-methylcyclopentane, m.p. 70° (picrate, m.p. 89°). (IV) is hydrogenated (PdO in $EtOH$) to almost equal amounts of (V) and (VI); with PdO in $EtOH$ containing alkali (V) is the sole product. (V) is reduced (Clemmensen) to trans-3-6'-methoxy-2'-naphthyl-2-methylcyclopentane, b.p. 110°/0.2 mm., m.p. 52—54° (picrate, m.p. 112°). H. W.

Preparation and pyrolysis of cyclohexanone. C. D. HURD, H. GREENGARD, and A. S. ROE (J. Amer. Chem. Soc., 1939, **61**, 3359—3360).—*cyclohexanone*, prepared in 60% yield by passing *cyclohexanol* over Cu chromite-pumice at 290—310°, gives no keten in a keten lamp. When passed over porcelain at 700—725°, it gives H₂O, *cyclohexadiene*, C₂H₄, CO, and some H₂ and CH₄. When boiled for 5 days, it gives 16% of *cyclohexylidenecyclohexanone*.

R. S. C.

Spiro-compounds. I. Preparation of cyclopentanespirocyclopentanone and cyclohexanespirocycloheptanone. M. QUDRAT-I-KHUDA and A. K. RAY. **II. Synthesis of cyclopentanespirocyclopentanone.** M. QUDRAT-I-KHUDA and A. MUKERJEE (J. Indian Chem. Soc., 1939, **16**, 525—531, 532—535).—I. *cyclopentanone* reduced with HgCl₂ and Mg or, better, Al in C₆H₆ yields 2-*cyclopentylidenecyclopentanone* together with di-1-hydroxy-1-*cyclopentyl*, m.p. 109°, which with 20% H₂SO₄ gives *cyclopentanespirocyclohexan-2-one* (CHPh: derivative, m.p. 75°), oxidised (HNO₃) to γ -1-*carboxy-1-cyclopentylbutyric acid* (I), m.p. 92°, the Et ester, b.p. 140—142°/6 mm., of which with EtOH-NaOEt affords *Et cyclopentanespirocyclopentan-2-one-3-carboxylate* (II), b.p. 127°/5 mm., hydrolysed (10% HCl) to *cyclopentanespirocyclopentan-2-one* (III), b.p. 115°/32 mm. (*semicarbazone*, m.p. 214°; CHPh: derivative, m.p. 64°). Di-1-hydroxy-1-*cyclohexyl* similarly yields *cyclohexanespirocycloheptan-2-one*, b.p. 120°/8 mm. (*semicarbazone*, m.p. 216—217°; CHPh: derivative, m.p. 123°), accompanied by much di- Δ^1 -*cyclohexene*. *cycloheptylidenecycloheptanone* with CN·CHN·CO·NH₂ yields a compound, C₁₃H₁₈O₂N₂, m.p. 215—216°.

II. Reduction of the anhydride of 1-carboxy-1-cyclopentylacetic acid yields the lactone, b.p. 154°/40 mm., of 1- β -hydroxyethylcyclopentane-1-carboxylic acid, which with PBr₅ followed by EtOH gives *Et 1- β -bromoethylcyclopentane-1-carboxylate*, b.p. 118°/5 mm. This with CHNa(CO₂Et)₂ provides *Et γ -1-carbethoxy-1-cyclopentylpropane- α -dicarboxylate*, b.p. 154°/6 mm., hydrolysed to (I) (*dianilide*, m.p. 163°), converted (as above) through (II) into (III), which is also obtained by heating (I) with Ba(OH)₂ and Fe powder.

F. R. G.

Stereoisomeric fuchsones. W. BOCKEMÜLLER and R. GEIER (Annalen, 1939, **542**, 185—203).—Fuchsones of type (A) exist in *cis*- and *trans*-forms.

4-*Methoxy-3-methyldiphenyl- α -naphthylcarbinol*, m.p. 131·5° [from 4:3:1-OMe·C₆H₃Me·COPh and 1-C₁₀H₇·MgBr (I) in Et₂O], and HCl in C₆H₆ give the *chloride*, two forms, m.p. 102—104° (slight decomp.) and ~155° (previous sintering and darkening); these eliminate MeCl at 110—130° (or in boiling PhCl) and 150—

200°, respectively, and afford 4-(*phenyl- α -naphthylmethylene*)-2-methyl- $\Delta^{2:5}$ -*cyclohexadienone* (II), m.p. 185—186°. *Phenyl- α -naphthyl-4-methoxy- α -naphthylcarbinol*, m.p. 224° [from 1:4-OMe·C₁₀H₆·COPh and (I)], with AcOH-HCl-AcCl at 100° (sealed tube) gives the *chloride*, m.p. 192° (decomp.), which at 200°/20 min. yields a substance, m.p. 217° (not the expected

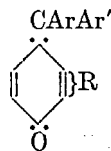
fuchsones; cf. below). Hydrolysis (aq. NaOH) of the product from *o*-cresol and *p*-C₆H₄Cl·CPhCl₂ at room temp./4 days affords 4-*chloro-4'-hydroxy-3'-methyltriphenylcarbinol*, m.p. 112—113° (previous sintering) (4'-*acetate*, m.p. 124—125°), dehydrated in boiling PhCl to 4-*p-chlorobenzhydrylidene-2-methyl- $\Delta^{2:5}$ -cyclohexadienone*, m.p. 133—134°. *o*-Cresol and 1-C₁₀H₇·CPhCl₂ (III) at 50—90° (occasionally better results obtained at room temp.—50°) give directly (II) and a labile *isomeride*, m.p. 156—157° (bath preheated to 155°) [subsequently resolidifying to (II)]; these forms are not polymorphs. α -C₁₀H₇·OH and (III) in C₆H₆ at room temp./2 days similarly yield (cf. above) 1-*keto-4-(phenyl- α -naphthylmethylene)-1:4-dihydronaphthalene*, forms, m.p. 197—198° (red melt) and 165° (preheated bath), resolidifying with m.p. 197—198°; a substance, decomp. >200°, is also formed. *p*-C₆H₄Ph·CPhCl₂ and α -C₁₀H₇·OH in C₆H₆ at 80° afford isomeric forms of 1-*keto-4-(phenyl- p -diphenylmethylene)-1:4-dihydronaphthalene*, m.p. 165—172° and 161—164°; both are reduced (Zn dust-AcOH or H₂, Pd-BaSO₄, EtOAc) to *phenyl- p -diphenyl-4-hydroxy- α -naphthylmethane*, m.p. 145—146°. Mesomerism is of little account in structures of type (A).

H. B.

Condensation of acenaphthenequinone with monohydric phenols. Cyclic pinacones and products of reduction and of auto-oxidation. H. BOGDAN (Bull. Acad. Sci. Roumaine, 1938, **20**, 26—27).—Acenaphthenequinone with *o*- and *m*-cresol, *o*- and *p*-xylenol, thymol, and α -C₁₀H₇·OH gives (cf. A., 1939, II, 20, 25) 8-keto-7:7-diarylacenaphthenes (A); *p*-cresol, *m*-xylenol, and β -C₁₀H₇·OH afford 7:8-dihydroxy-7:8-diarylacenaphthenes which with conc. H₂SO₄ yield anhydroderivatives (xanthenes). Reduction (Zn, alkali) of (A) gives the 8-OH-derivatives which undergo autoxidation to coloured products (act as indicators).

J. L. D.

$\alpha\beta$ -Diacylethylene glycols. R. C. FUSON, C. H. MCBURNEY, and W. E. HOLLAND (J. Amer. Chem. Soc., 1939, **61**, 3246—3249).—Formation of [RCO·CH(OH)]₂ from RCO·CHO by Mg + MgI₂ (Gomberg *et al.*, A., 1927, 245) is a general reaction, but the yield depends on the ratio of Et₂O to C₆H₆ used as solvent and on the reaction time. 3:5-*Dibromomesitylglyoxal* (prep. in 41·5% yield from 2:4:6:3:5:1-C₆Me₃Br₂·COMe by SeO₂ in wet dioxan), b.p. 157°/4 mm. or, +H₂O, m.p. 100—102° (*semicarbazone*, m.p. 238—241°; *phenylhydrazone*, m.p. 183—184·5°), with 10% NaOH gives 3:5-*dibromomesitylglycollic acid*, m.p. 184—185°, and with Mg + MgI₂ in Et₂O·C₆H₆ (17:25) gives 27% of $\alpha\delta$ -*diketo- $\alpha\delta$ -di-3:5-dibromomesitylbutane- $\beta\gamma$ -diol*, m.p. 229—232°. *isoDurylglyoxal* (prep. in 72% yield from acetoisodurene by SeO₂), b.p. 123—127°/8 mm. or, +H₂O, m.p. 86—87° (*semicarbazone*, m.p. 207—208°; *phenylhydrazone*, m.p. 118—119°), gives similarly *iso-durylglycollic acid*, m.p. 171·5—172° (lit. 156°), and $\alpha\delta$ -*diketo- $\alpha\delta$ -diisodurylbutane- $\beta\gamma$ -diol*, m.p. 160—161°. The appropriate glyoxals similarly give $\alpha\delta$ -*diketo- $\alpha\delta$ -di-2:4:6-triethylphenylbutane- $\beta\gamma$ -diol*, m.p. 104—105° (corr.), and [Bu'CO·CH(OH)]₂. BzCHO gives diastereoisomeric forms, m.p. 126—127·5° (corr.) [*di*-



(A.)

acetate, m.p. 168—169° (corr.) and 118—119° (corr.), of $\alpha\delta$ -diketo- $\alpha\delta$ -diphenylbutane- $\beta\gamma$ -diol; the yield is 55% in 2:3 but only 2% in 1:2 Et₂O-C₆H₆. When heated with Mg + MgI₂ for 15 min., mesitylgllyoxal gives $\alpha\delta$ -diketo- $\alpha\delta$ -dimesitylbutane- $\beta\gamma$ -diol (I), but after 1 hr. some dimesitylformoin (II) is also obtained. 2:4:6-C₆H₂Me₃·CO·COPh and Mg + MgI₂ give C₆H₂Me₃·CO·CHPh·OH. (I) gives a CMe₃ ether, m.p. 117—118°, is oxidised by CuSO₄-C₅H₅N to (2:4:6-C₆H₂Me₃·CO)₂, by SeO₂ in wet dioxan to CO(CO·C₆H₂Me₃-2:4:6)₂ (in both cases probably by way of the tetraketone), and by Pb(OAc)₄ in CHCl₃ to mesitylgllyoxal [phenylhydrazone, m.p. 136—137.5° (corr.) (lit. 145—146°)], and with EtOH-NHPh·NH₂ at 100° gives a compound, C₂₃H₂₂O₂N₂, m.p. 128—129° (corr.). With H₂C₂O₄·2H₂O at 160°, conc. H₂SO₄ at 0°, or NaOEt at room temp., (I) gives 2:4:6-C₆H₂Me₃·CO·CH·C(OH)·CO·C₆H₂Me₃-2:4:6 (III). Attempts to prepare tetra-acyl derivatives of (I) failed; MgEtBr (4 mols.), followed by AcCl, gives (II); boiling BzCl gives the benzoate of (III); boiling Ac₂O-NaOAc gives an oil. R. S. C.

Triketohydrindyl- (ninhydril-) and alloxanyl-carbamides and their constitutions. M. POLONOVSKI, P. GONNARD, and (MLLE.) G. GLOTZ (Bull. Soc. chim., 1939, [v], 6, 1557—1576).—Triketohydrindene hydrate (ninhydrin) and the respective NH₂·CO·NRR' in H₂O (bath) give *ninhydril-methyl-*, m.p. 230°, *-dimethyl-*, m.p. ~260° (decomp.), and *-phenyl-carbamide*, m.p. 105° (decomp.), but no reaction is obtained with CO(NHR)₂. Ninhydril-carbamide is probably C₆H₄<CO>C<OH>N·C(OH)·NH₂.

Contrary to Biltz *et al.* (A., 1912, i, 589; 1921, i, 616), 5-carbamido-5-hydroxybarbituric acids are probably formed from alloxan (I); the 5-*phenyl-*, decomp. ~180—185°, and 5-N'N'-*dimethyl-carbamido-* (II) -derivative, decomp. ~180—181° (red at 150°), can be prepared. In EtOH, H₂O, or 0.1N-HCl, (I) and (II) are probably mainly in the keto-form; at $pH > 7$, (II) probably undergoes fission to (I) and NH₂·CO·NMe₂. The absorption spectra of the above and allied compounds are compared with those of barbituric acid and its 5-NO₂-derivative, uric and ϕ -uric acid, uramil, aminouramil,

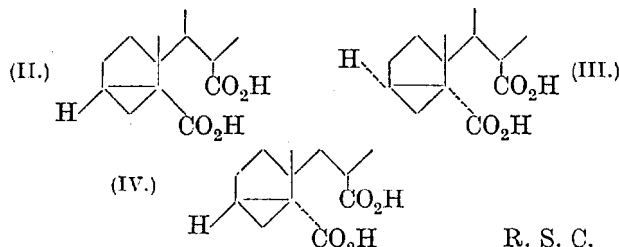
NH₂·CO·NH·CH₂·CO·CN, and CO<NH·CO>C·NH₂.

A. T. P.

Steroid ketones.—See B., 1940, 172.

Molecular rearrangements in sterols. IV. Structure of *i*-cholestanone. K. LADENBURG, P. N. CHAKRAYORTY, and E. S. WALLIS (J. Amer. Chem. Soc., 1939, 61, 3483—3487; cf. A., 1938, II, 137).—The following experiments support the presence of a cyclopropane ring in *i*-cholesterol. Its stability depends on the state of oxidation of C₆. *i*-Cholestanone (I), m.p. 96° [prep. from the oxime, m.p. 143—144° (lit. 122—123°)], suffers ring-fission with H₂SO₄-AcOH, giving β -3-hydroxycholestan-6-one (oxime, m.p. 194—195°, of the acetate), and with 34% HBr and AcOH at room temp. gives α -3-bromocholestan-6-one, m.p. 123°, converted by boiling quinoline in N₂ into Δ^4 -cholesten-6-one, m.p. 104—105°

(oxime, m.p. 184—185°). KOB₂ oxidises (I) to α_1 -*i*-cholestan-6:7-diacid (II), m.p. 232—233°, [α]_D²⁵ +18° in abs. COMe₂. β -3-Chlorocholestan-6:7-diacid, m.p. 243°, and NaOEt-EtOH at 120° give β_2 -*i*-cholestan-6:7-diacid (III), m.p. 230—231°, [α]_D²⁴ +55° in abs. COMe₂; α -3-chlorocholestan-6:7-diacid gives similarly α_2 -*i*-cholestan-6:7-diacid (IV), m.p. 265°, [α]_D²⁵ +46° in dioxan.



R. S. C.

Transformations of brominated derivatives of cholesterol. VI. Constitution of $\Delta^{1:2-4:5}$ -cholestadien-3-one. H. H. INHOFFEN and HUANG-MINLON (Ber., 1939, 72, [B], 1686—1687; cf. A., 1938, II, 413).—Hydrogenation (Pd sponge in Et₂O) of the ketocarboxylic acid, C₂₆H₄₂O₃, obtained by the ozonisation of $\Delta^{1:2-4:5}$ -cholestadien-3-one (I) (derived from 2:4-dibromocholestanone and C₅H₅N) gives the acid, C₂₆H₄₄O₃, m.p. 153—154° (oxime, m.p. 189—190°), identical with that obtained by Windaus (A., 1906, i, 579) and by Dorée *et al.* (J.C.S., 1908, 93, 1330) from cholestenone. The non-cryst. neutral ozonisation product of (I) gives a semicarbazone, C₂₄H₄₂ON₃, m.p. 224—225° (decomp.). H. W.

3-Hydroxyandrostene methyl ketimine.—See B., 1940, 172.

Sterols. LXXXVI. Deoxotestosterone and its conversion into testosterone. R. E. MARKER, E. L. WITTE, and B. F. TULLAR (J. Amer. Chem. Soc., 1940, 62, 223—226).—Oxidation of $\Delta^{5:6}$ -cholestene dibromide by CrO₃-AcOH at 48—50° and subsequent debromination yields $\Delta^{5:6}$ -androst-17-one, m.p. 105—107° (isolated as semicarbazone, m.p. 285—287°), which with Na-Pr^oOH gives $\Delta^{5:6}$ -androst-17-ol (I), m.p. 163—165° (acetate, m.p. 133—135°). Conversion into the hydrochloride by HCl-CHCl₃ at 0° and refluxing thereof with KOAc-EtOH partly isomerises (I) to $\Delta^{4:5}$ -androst-17-ol (II), m.p. 146—149° [separated from (I) as its acetate (III), m.p. 97—100°; does not depress the m.p. of (I)], oxidised by CrO₃-AcOH (protection as dibromide) to $\Delta^{4:5}$ -androst-17-one, m.p. 78—80°. Oxidation of (III) by CrO₃-AcOH at 50°, separation of the ketones by Girard's reagent, hydrolysis thereof by warm HCl-EtOH, and distillation at 0.01 mm. yields testosterone. If impure (III) is used, some 7-keto- $\Delta^{5:6}$ -androst-17-yl acetate, m.p. 215—217°, is obtained. This yields 7-keto- $\Delta^{5:6}$ -androst-17-ol, m.p. 141.5—142.5° (2:4-dinitrophenylhydrazones, m.p. 230—232°). CrO₃-AcOH at 35—45° oxidises (II) to androstenedione.

R. S. C.

Sterols. LXXXII. Oestrane derivatives. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 73—75).—Contrary to Butenandt (A., 1930, 1480), hydrogenation (PtO₂) of oestrone in abs. EtOH at room temp./3 atm. gives 90% of α -oestradiol

(I), m.p. 173—175°. Cestrane-3:17-dione [obtained with non-cryst. cestranolones (A) from cestrane-3:17(α)-diol and CrO_3], forms, m.p. 144—146° and 179—180°, and Br-HBr-AcOH give a Br-derivative, m.p. 170—172°, converted by boiling $\text{C}_5\text{H}_5\text{N}$ into (? Δ^4 :5)-*æstrene*-3:17-dione, m.p. 146—148°. Hydrogenation (PtO_2) of (A) in HCl-MeOH at 25°/2 atm. gives *æstran*-17(α)-ol (II), identical with the product obtained also from *æstrone*. The 17-acetate of (I), prepared from the diacetate by K_2CO_3 -MeOH at 20°, with H_2 -PtO₂ in EtOH-AcOH at 10 lb. gives a product, which by oxidation and hydrolysis yields an *æstran*-17-ol-3-one, m.p. 102—104° (reacts with Br, but yields no nortestosterone) and (II). R. S. C.

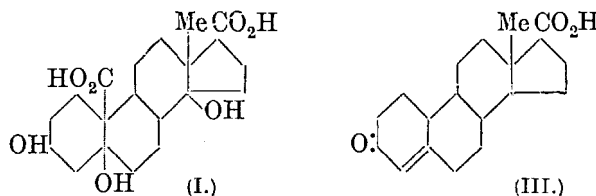
Sterols. LXXVI. Oxidation and reduction products of equilenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 3314—3317).—Hydrogenation (PtO_2) of equilenin in abs. EtOH-Et₂O at 25°/3 atm. gives α -dihydroequilenin, further hydrogenation of which in HCl-EtOH gives Δ^5 :10-6:7-8:9-*æstratrien*-17(α)-ol (I) (A., 1937, II, 250) (proof of α -OH), which is oxidised by CrO_3 -AcOH at 25° to Δ^5 :10-6:7-8:9-*æstratrien*-17-one, m.p. 107—109° [oxime, m.p. 203—205° (decomp.)]. The diketone (II), $\text{C}_{18}\text{H}_{16}\text{O}_2$, of Marker *et al.* (A., 1940, III, 32) is probably 11-*keto*-3-*deoxyequilenin*; with H_2 -PtO₂-HCl-EtOH it gives (I), with H_2 -PtO₂-abs. EtOH-Et₂O gives the (?) 11:17-*diol*, $\text{C}_{18}\text{H}_{20}\text{O}_2$, m.p. 209—212°, with Zn-HCl-EtOH gives a *monoketone*, $\text{C}_{18}\text{H}_{18}\text{O}$, m.p. 156—158°, and with Zn-Hg-HCl-EtOH gives *deoxyequilenin*, $\text{C}_{18}\text{H}_{20}$, m.p. 73—75°. Equilenin acetate and CrO_3 -80% AcOH at 25° give 11-*keto*equilenin acetate, m.p. 195—197° [*semicarbazone*, m.p. 238—241° (decomp.)], whence it is probable that the natural precursor of (II) has no 11-CO. Hydrogenation (PtO_2) of *equilenin*-3-*oxyacetic acid*, m.p. 233—236° (Me, m.p. 180—182°, and ? Et ester, m.p. 141.5—143°), in HCl-EtOH gives (I).

R. S. C.

Preparation and properties of 3(α):11-dihydroxy-12-ketocholanic acid. B. B. LONGWELL and O. WINTERSTEINER (J. Amer. Chem. Soc., 1940, 62, 200—203).—Some of the following experiments contradict results of Marker *et al.* (A., 1938, II, 329). When 3-hydroxy-12-ketocholanic acid, m.p. 162—163° (acetate, m.p. 197—198°), is boiled in Ac_2O -AcOH and then treated with Br-AcOH at 50—60°, it gives 11-bromo-12-*keto*-3(α)-*acetoxycholanic acid* (I), amorphous, m.p. 159° (decomp.), hydrolysed by 20% KOH-MeOH to 3(α):11-dihydroxy-12-ketocholanic acid (II), m.p. 205°, $[\alpha]_D^{25} + 67.1^\circ$ in 95% EtOH [Me ester, m.p. 157° (*H succinate*, m.p. 194—196°); *diformate*, m.p. 146—148°]. With Ac_2O - $\text{C}_5\text{H}_5\text{N}$, (II) gives the gummy *diacetate*, but with boiling Ac_2O gives mainly (?) an *anhydride* (III), $\text{C}_{26}\text{H}_{40}\text{O}_{10}$, m.p. 268° [hydrolysed to (II)]; boiling 33% AcOH converts (III) into the 3-*acetate* (+0.5 H_2O), m.p. 106°, of (II). With NaOAc in AcOH at 185—190°, (I) gives 12-*keto*-3(α)-*acetoxyl*- Δ^9 :11-*cholenic acid*, m.p. 201°. (II) gives no CO-derivatives and with N_2H_4 -NaOEt-EtOH at 197—200° suffers dehydration as well as reduction, yielding a substance, $\text{C}_{24}\text{H}_{38}\text{O}_3$, +0.5 H_2O , m.p. 162—163° [*H succinate*, m.p. 227° (decomp.)].

R. S. C.

Experimental connexion of the vegetable heart poisons with the *æstrone* group. A. BUTENANDT and T. F. GALLAGHER (Ber., 1939, 72, [B], 1866—1869).—Strophanthidin, m.p. 176°, is converted into the acid (I), which is dehydrated by boiling 0.1N-HCl-EtOH to the *anhydrodicarboxylic acid*, $\text{C}_{20}\text{H}_{28}\text{O}_6$, decomp. 260° after softening and darkening at 250° according to rate of heating, $[\alpha]_D^{25} + 122^\circ$ in EtOH (*Me*₂ ester, m.p. 150°, $[\alpha]_D^{25} + 108^\circ$ in abs. EtOH).



This is hydrogenated to the saturated acid, $\text{C}_{20}\text{H}_{30}\text{O}_6$, decomp. 255—256°, $[\alpha]_D^{15} + 35^\circ$ in abs. EtOH [*Me*₂ ester, m.p. 164—165° (decomp.)], which is oxidised (CrO_3 in AcOH) to the *ketodicarboxylic acid* (II), $\text{C}_{20}\text{H}_{28}\text{O}_6$, m.p. 193—194° (decomp.). (II) is transformed by HCl in boiling MeOH into 3-*keto*- Δ^4 -*æstrene*-17-*carboxylic acid* (III), m.p. 186°, $[\alpha]_D^{25} + 83^\circ$ in abs. EtOH. H. W.

Sterols. LXXIX. Oxidation products of dihydrosarsasapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 3477—3479).—Dihydrosarsasapogenin diacetate and CrO_3 -AcOH at 90—95° give a syrup, hydrolysed to the lactone, $\text{C}_{22}\text{H}_{34}\text{O}_3$, the keto-acid (I), $\text{C}_{22}\text{H}_{34}\text{O}_4$, and the acid, $\text{C}_{17}\text{H}_{28}\text{O}(\text{CO}_2\text{H})_2$. Me anhydrotetrahydrosarsasapogenoate acetate and CrO_3 -AcOH at 55—60° (later 80°) give a mixture, hydrolysed to anhydrosarsasapogenoic acid, (I), and 3-hydroxyætiobilanic acid. These reactions support the authors' formulæ (A., 1939, II, 276, 510).

R. S. C.

Sterols. LXXXIII. Oxidation products of sarsasapogenin. The C_{22} -lactone. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 76—78).—The C_{22} -lactone (I), m.p. 199—200°, from sarsasapogenin with HI and H_3PO_4 gives gums, and with CrO_3 -AcOH at 50—55° gives an acid, $\text{C}_{20}\text{H}_{30}\text{O}_2(\text{CO}_2\text{H})_2$, m.p. 285—288° (decomp.) (*Me*₂ ester, m.p. 170—171.5°) (cf. Simpson *et al.*, A., 1935, 864), also obtained from sarsasapogenone by HNO_3 (d 1.5) in AcOH at 90°. CrO_3 -AcOH at 90° oxidises the acetate of (I) to a product, hydrolysed to a CO-acid (II), $\text{C}_{22}\text{H}_{34}\text{O}_4$, m.p. 285—287° (decomp.) [*Me* ester acetate, m.p. 198—199.5°; *oxime*, m.p. 206—208° (decomp.)]. MgPhBr in Et₂O converts (I) into a carbinol, which by successive acetylation, oxidation (CrO_3), and hydrolysis yields the known (?) 3-hydroxyætiobilanic acid, $\text{C}_{19}\text{H}_{30}\text{O}_5$, m.p. 218—220°. Hydrogenation of (II) in EtOH-HCl gives (I) [m.p. 186—188°; polymorphism (cf. A., 1939, II, 322)], oxidised (CrO_3) to the 3-CO-lactone, m.p. 184—185°, which with H_2 -PtO₂ in 98% EtOH at 3 atm. affords an *epilactone*, $\text{C}_{22}\text{H}_{34}\text{O}_3$, m.p. 198—200° (acetate, m.p. 159—160°).

R. S. C.

Steroids and related compounds. V. Steroid diosphenols. V. A. PETROW and W. W. STARLING (J.C.S., 1940, 60—65).—*cis*- Δ^5 -Cholestene-3:4-diol dibromide is oxidised (H_2CrO_4 in aq. AcOH + C_6H_6 at

room temp.) and debrominated (NaI) to Δ^5 -cholestene-3:4-dione, form A (I), (+0.5H₂O), m.p. 135—136°, $[\alpha]_D^{25} + 30.5^\circ$, acetylated to 4-acetoxy- Δ^4 -cholestadien-3-one, and oxidised (H₂O₂, aq. EtOH-KOH) to Diels' acid. *cis*- Δ^5 -cholestene-3:4-diol is acetylated (Ac₂O-C₂H₅N) to *cis*-3-acetoxy- Δ^5 -cholesten-4-ol, m.p. 193—194°, $[\alpha]_D^{25} - 64.5^\circ$, which is oxidised (H₂CrO₄-aq. AcOH + C₆H₆) to 3-acetoxycholestan-4-one 5:6-oxide (II), m.p. 173—174°, $[\alpha]_D^{25} + 3.8^\circ$ (corresponding 3-benzoyloxy-compound, m.p. 185—186°, $[\alpha]_D^{25} + 6.4^\circ$). Boiling AcOH-NaOAc or EtOH-C₆H₆-conc. HCl converts (II) into Δ^5 -cholestene-3:4-dione, form B (III), m.p. 162—163°, $[\alpha]_D^{25} + 57.3^\circ$, also obtained from (I) and warm AcOH-conc. HCl. (I) and (III) yield the same quinoxaline, m.p. 175° (different conditions necessary), and *mono*-2:4-dinitrophenylhydrazone, m.p. 255°. (I) is labile and the change to the stable form (III) is non-reversible. (I) is the diketomodification and (III) is $\Delta^{2:5}$ -cholestadien-3-ol-4-one; (III) is evidently identical with the substance obtained by debromination of 5:6:4:4'-tetrabromocholestan-3-one (Butenandt *et al.*, A., 1936, 1512).

cis-3-Acetoxy- Δ^5 -cholesten-4-ol dibromide, m.p. 115°, is oxidised to 3-acetoxy- Δ^5 -cholesten-4-one, m.p. 123—124°, $[\alpha]_D^{25} - 76.7^\circ$ (whence 3:4-diacetoxy- $\Delta^{3:5}$ -cholestadiene, m.p. 128°), which is converted by EtOH-conc. HCl into cholestane-3:4-dione, m.p. 149—150°, $[\alpha]_D^{25} + 79.7^\circ$ (cf. Butenandt *et al.*, A., 1937, II, 63). Only one form of this ketone has been obtained; it yields a quinoxaline derivative, m.p. 208—209°, a *mono*-2:4-dinitrophenylhydrazone, m.p. 252—253°, an enol acetate, m.p. 102—103°, $[\alpha]_D^{25} + 92.5^\circ$; and is oxidised to cholestane-C₃||C₄-diacid (dihydro-Diels' acid). NaOEt in Et₂O-EtOH and (II) give $\Delta^{2:5}$ -cholestadien-3-ol-4-onyl-6:6'-($\Delta^{4:6'}$ -cholestadien-4-ol-3'-one), m.p. 239—240°, $[\alpha]_D^{25} + 23.7^\circ$ [*mono*-2:4-dinitrophenylhydrazone, m.p. 248° (decomp.); diacetate, m.p. 205—206°, $[\alpha]_D^{25} - 52.4^\circ$]. 4-Acetoxy- $\Delta^{4:6}$ -cholestadien-3-one, m.p. 161—162°, is obtained from (II) and Ac₂O-NaOAc. All rotations are in CHCl₃. M.p. are corr. F. R. S.

Sterols. LXXXIV. Progesterone from hyodeoxycholic acid. R. E. MARKER and J. KRUEGER (J. Amer. Chem. Soc., 1940, 62, 79—81).—6-Ketocholestanol and H₂-PtO₂ in MeOH at 3 atm. give cholestane-3:6-diol, m.p. 190° [stereoisomeric with that described by Windaus (A., 1917, i, 265)], the diacetate, m.p. 138°, of which with KOH-MeOH at 20° or boiling NaHCO₃-MeOH and a little H₂O gives the 6-monoacetate, oxidised by CrO₃ in AcOH at room temp. to 6-acetoxycholestan-3-one, m.p. 101°. Boiling 2% KOH-MeOH then gives 6-hydroxycholestan-3-one, m.p. 190°, which, when distilled with KHSO₄, yields cholestenone. *Me hyodeoxycholate*, m.p. 86°, is converted by way of the diphenylcarbinol into *norhyodeoxycholic acid*, m.p. 198° (*Me* ester, +C₆H₆, m.p. 95°), and thence similarly into the *diphenylcarbinol*, C₂₅H₃₅O₃, m.p. 222°, and *bisnorhyodeoxycholic acid*, m.p. 240°. The *Me* ester (CH₂N₂), m.p. 146°, thereof with MgPhBr etc. yields an alcohol, the acetate of which in boiling AcOH followed by O₃ in CHCl₃ gives 3:6-diacetoxy α -tiocholanyl *Me* ketone, m.p. 100°. Half-hydrolysis, oxidation, hydrolysis, and dehydration as described above then gives progesterone. R. S. C.

Action of lead tetra-acetate on ketones of the pregnane series. II. G. EHRHART, H. RUSCHIG, and W. AUMÜLLER (Ber., 1939, 72, [B], 2035—2039; cf. A., 1939, II, 327; Reichstein *et al.*, A., 1939, II, 552).—Progesterone (I), like pregnenolone acetate, is attacked by Pb(OAc)₄ at C₂₁; instead of or simultaneously with this action an OAc group can be introduced into the ring structure. (I) is converted by Pb(OAc)₄ in AcOH at 75—85° into a non-cryst. product (II) from the solution of which in EtOH diacetoxyprogesterone, m.p. 198°, $[\alpha]_D^{25} + 164.6^\circ \pm 2^\circ$ in EtOH, separates. It is hydrolysed (KHCO₃ in aq. MeOH) to dihydroxyprogesterone, m.p. 184°, which is oxidised (HIO₄ in aq. MeOH at room temp.) to (2?)-hydroxy-3-keto α -tiocholonic acid, m.p. 254°. Hydrolysis of (II) gives a crude hydroxyprogesterone, m.p. ~134° after softening at 115°, which when dissolved in Et₂O and shaken with NaOH yields an unidentified substance, m.p. 191—192°. Chromatographic treatment of the neutral solution gives hydroxyprogestones, m.p. 185°, $[\alpha]_D^{25} + 186^\circ \pm 10^\circ$ in EtOH (acetate, m.p. 198°), and m.p. 184°, $[\alpha]_D^{25} + 40^\circ \pm 10^\circ$ in EtOH. H. W.

Halogeno- and amino-alkoxy-*p*-benzoquinones.—See B., 1940, 118.

Synthesis of vitamin-K₁. L. F. FIESER [and, in part, M. D. GATES] (J. Amer. Chem. Soc., 1939, 61, 3467—3475).—Partly a detailed account of work already reported (A., 1939, II, 513). Isolation of vitamin-K₁ from lucerne concentrates is greatly simplified by using the quinol form. Phthiocol is isolated after application of the Dam-Karrer reaction to -K₁. 2:6-Dimethyl-3-phytyl-1:4-naphthaquinol diacetate has m.p. 55—56.5°. 2-Ethyl-3-phytyl-1:4-naphthaquinone, which is synthesised, differs from -K₁ in solubility, and in having no -K-activity at 160 μ g. The min. dose of -K₁ is 2 μ g. 2:6-Dimethyl-3-phytyl-1:4-naphthaquinone (absorption max. at 247, 256.5, 264.5, 271, and 331 m μ) is inactive in 50- μ g. doses. A 25- but not a 5- μ g. dose of 2-methyl-3-geranyl-1:4-naphthaquinone is effective. The great, but varying, activity of 2-methyl-1:4-naphthaquinone may be due to its use for synthesis of -K in the body. R. S. C.

Ultra-violet absorption of vitamin-K₁, -K₂, and related compounds.—See A., 1940, III, 146.

Diene synthesis of 2:3-dialkyl-1:4-naphthaquinones related to vitamin-K. L. F. FIESER and (Miss) C. W. WIEGHARD (J. Amer. Chem. Soc., 1940, 62, 153—155).—CMe₂:CH-COMe (I) and MgMeCl in hot Et₂O give CMe₂:CH-CMe:CH₂, which, when boiled with α -naphthaquinone (II), gives 1:1:3-trimethyl-1:4:11:12-tetrahydroanthraquinone, m.p. 119°. Isomerisation by hot KOH-EtOH and subsequent oxidation by air then gives 1:1:3-trimethyl-1:4-dihydroanthraquinone, m.p. 129—129.5° (Diels *et al.*, A., 1929, 1303, m.p. 162°). MgBu^tCl gives similarly CMe₂:CH-CBu^t:CH₂, b.p. 58—59°/32 mm., 1:1-dimethyl-3-tert-butyl-1:4:11:12-tetra- (13%), m.p. 142—143°, and -1:4-di-hydroanthraquinone (III), m.p. 102—103°. Similar syntheses using MgEtBr failed, probably owing to the initial product of interaction with (I) undergoing dehydration

in two directions. Myrcene and (II) in boiling dioxan give 2-*δ*-methyl- Δ^7 -*n*-pentenyl-1 : 4 : 11 : 12-tetrahydroanthraquinone (64%), m.p. 61—61.3° (lit. 58—58.5°), converted by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ into 9 : 10-diacetoxy-2-*δ*-methyl- Δ^7 -*n*-pentenyl-1 : 4-dihydroanthracene, m.p. 121—122°; treatment with MgMeCl in Et_2O (later boiling C_6H_6) and oxidation by $\text{Ag}_2\text{O}-\text{Na}_2\text{SO}_4$ in C_6H_6 then give 2-*δ*-methyl- Δ^7 -*n*-pentenyl-1 : 4-dihydroanthraquinone (IV), m.p. 89.8—90.8°. In 400- and 50- μg . doses, respectively, (III) and (IV) have no vitamin-K activity. M.p. are corr. R. S. C.

2-*o*-Aminophenylanthraquinone and 1 : 2-phthaloylcarbazole. P. H. GROGGINS (Ind. Eng. Chem., 1940, 32, 98).—2-*o*-Chlorophenylanthraquinone with aq. $\text{NH}_3-\text{PhNO}_2-\text{Cu}$ catalyst yields (cf. A., 1930, 1186) 1 : 2-phthaloylcarbazole, m.p. 255°, and little 2-*o*-aminophenylanthraquinone.

J. D. R.

Essential oil from rhizome of *Acorus calamus*. I. Isolation and examination of calamol. M. QUDRAT-I-KHUDA, A. MUKHERJEE, and S. K. GHOSH (J. Indian Chem. Soc., 1939, 16, 583—588).—Steam-distillation of the rhizome of *A. calamus* gives 7.9% of oil consisting mainly of a trimethoxyallylbenzene derivative, calamol (I), $\text{C}_{12}\text{H}_{16}\text{O}_3$, b.p. 153—154°/5 mm., $[\text{R}_L]_D$ 61.9, giving with $\text{EtOH}-\text{KOH}$ isocalamol (II), b.p. 133°/2 mm., $[\text{R}_L]_D$ 61.85. (I) gives with $\text{Br}-\text{C}_6\text{H}_4\text{O}_3\text{Br}_4$ (impure), with H_2-PdCl_2 , dihydrocalamol, $\text{C}_{12}\text{H}_{18}\text{O}_3$, b.p. 124°/2 mm., $[\text{R}_L]_D$ 61.1, with AlCl_3 a phenol, $\text{C}_{11}\text{H}_{14}\text{O}_3$, b.p. 115°/2 mm., with HI an impure product, which gives a Bz_3 derivative, $\text{C}_{30}\text{H}_{22}\text{O}_6$, m.p. 96°. Oxidation of (I) and (II) with cold KMnO_4 in aq. NaOH gives calamonic acid, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CO}_2\text{H}$, m.p. 143°, which gives with HI a trihydroxybenzoic acid, $\text{C}_7\text{H}_6\text{O}_5$, m.p. 97°. T. F. W.

Complex metallic salts of semicarbazone and oxime of 8-oximinaminomenthone. M. BRAMBILLA (Annali Chim. Appl., 1939, 29, 513—523).—Pulegonehydroxylamine, m.p. 143° (cf. Beckmann and Pleissner, A., 1891, 936), with HNO_2 gives 8-oximinaminomenthone (pulegonenitrosohydroxylamine) {semicarbazone (I), m.p. 165° (Na salt, m.p. 235°; K salt, m.p. 75°, then 110°; NH_4 salt, m.p. 154—156°); oxime (II), m.p. 76° (Na salt, m.p. 219°, $[\text{+}4\text{H}_2\text{O}$, m.p. 64.5°), K salt, m.p. 267° [decomp.]; NH_4 salt, m.p. $\sim 80^\circ$ }. Pptn. reactions of (I) and (II) with aq. salts of Cu , Ni , Cd , Mn , Zn , Fe , Hg , Co , Pb , Al , and Cr and solubilities of the complexes in H_2O , EtOH , and Et_2O are tabulated. The pptn. of Cu and Cd by (I) and (II) is quant. The structure of the metallic complexes is discussed. F. O. H.

Constitution of two new terpenes, menogene and menogerene ($\text{C}_{10}\text{H}_{16}$ and $\text{C}_{10}\text{H}_{14}$). Mechanism of cyclisation of citronellal and citral. R. HORIUCHI, H. OTSUKI, and O. OKUDA (Bull. Chem. Soc. Japan, 1939, 14, 501—507).—Citronellal and 50% H_2SO_4 give menogene (I), $\text{C}_{10}\text{H}_{16}$, b.p. 184—186°/764.5 mm., $[\alpha]_D^{25} + 49.11^\circ$ (nitrosite, m.p. 154.5—155°), reduced by H_2-PdO to *p*-menthane, and converted by maleic anhydride into the adduct, m.p. 205—208° (dibromide, m.p. 282—285°). When heated with Na , (I) yields COMe_2 . (I) is probably $\Delta^{2:4(8)}$ -*p*-menthadiene, and is formed from citronellal via 3-hydroxy- $\Delta^{8(9)}$ -*p*-menthene and 3 : 8-dihydroxy-*p*-

menthane. Distillation of the product from citral and 20% H_2SO_4 yields COMe_2 , 1-methyl- $\Delta^{1:5}$ -cyclohexadiene, b.p. 110—111°, *p*-cymene, (I), and menogerene (II), $\text{C}_{10}\text{H}_{14}$, b.p. 180—181°. (II) affords a dibromide, m.p. 114.5—115°, and when distilled after long keeping or when treated with 20% H_2SO_4 yields (I). With H_2-Pd it gives *p*-menthane and *dl*- α -phellandrene. (II) is therefore probably $\Delta^{1:5:4(8)}$ -*p*-menthatriene, and citral cyclises to (II) through 3-hydroxy- $\Delta^{1:8(9)}$ -*p*-menthadiene and 1 : 3 : 8-trihydroxy-*p*-menthane.

J. D. R.

Pinane group. VII. Total synthesis of verbenone. Total synthesis of α - and β -pinene. P. C. GUHA and P. L. N. RAO (J. Indian Inst. Sci., 1939, 22, A, 326—330).—Verbanone (I) and SeO_2 in boiling 96% EtOH for 12 hr. give verbenone (II); since (I) has been synthesised (cf. Komppa *et al.*, A., 1937, II, 252) and (II) has been converted into α -pinene (III) (cf. Blumann *et al.*, A., 1921, i, 426; Ruzicka *et al.*, A., 1924, i, 755), a total synthesis of (III) has been accomplished. Verbenene, free from (III), gives (III) when reduced with Na in EtOH . (III) with KMnO_4 gives pinonic acid, isolated as the semicarbazone (cf. Blumann *et al.*, *loc. cit.*).

J. L. D.

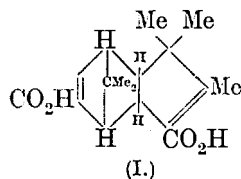
Camphorone and pulegone. Hydrogenation products and their structure. IV. Hydrogenation in presence of metallic catalysts. V. *cis*- and *trans*-Dihydrocamphorones. VI. Hydrogenation of dihydrocamphorones; conversion of *trans*- into *cis*-ketone. VII. Dehydration of dihydrocamphorols; structure of corresponding ketone. R. CALAS (Bull. Soc. chim., 1939, [v], 6, 1485—1493, 1493—1498, 1499—1505, 1505—1510; cf. A., 1939, II, 483).—IV, V. Hydrogenation (Pt) (6 min. for 1 mol. H_2) of camphorone (I) or pulegone (II) (more slowly) affords in AcOH , or more rapidly in EtOH , respectively, *cis*- (III), b.p. 70°/14 mm. (oxime, new m.p. 76—77°; carbanilide-oxime, m.p. 142°), or *trans*- (IV) dihydrocamphorone, b.p. 70°/14 mm. (oxime, b.p. 117°/16 mm.; carbanilide-oxime, m.p. 139°), respectively, purified through the respective semicarbazone, m.p. 198° or 209° (cf. A., 1938, II, 100). Hydrogenation of (I) and (II), using $\text{Pt}-\text{Fe}$ (Faillebin, A., 1926, 50) in EtOAc , gives (IV), with no further hydrogenation (cf. Pt). (IV) oximates more quickly. Physical consts. are recorded. The literature of dihydrocamphorones is clarified.

VI, VII. (III) or (IV) (more readily) and Na in aq. $\text{Et}_2\text{O}-\text{NaHCO}_3$ or EtOH give *cis*- + *trans*-dihydrocamphorols of the *cis*-ketone (H phthalates, m.p. 114° and 84°, respectively); either is dehydrated by $\text{o}-\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 130—140° to 1-methyl-3-isopropyl- Δ^1 -cyclopentene, b.p. 138—139°/757 mm. (nitrosochloride, m.p. 119°; nitrolpiperidide, m.p. 161°). Enolisation probably precedes reduction; cnolisation (MgPr^{Br}) of (III) or (IV) gives 17—18% of enol. After decomp. of the Mg compound, (III) only is recovered from (III), but (IV) gives (IV) + 15% of (III), i.e., enol form gives *cis*-ketone. Mechanisms of hydrogenation and other theoretical aspects are discussed. A. T. P.

ω -Camphor series. I. Synthesis of 2-keto-apocamphane-1-acetic acid. T. HASSELSTROM and

B. L. HAMPTON (J. Amer. Chem. Soc., 1939, **61**, 3445—3448).—The oxime, new m.p. 160—161°, of ω -benzoylborneol (new m.p. 86—87°) with PCl_5 in Et_2O gives 2-hydroxyapocamphane-1-acetanilide (I) (28.2%), m.p. 176.5—177.5°, camphenecarboxyanilide (II) (10.1%), m.p. 154.5—155.5° (formed by Meerwein-Wagner retropinacolin rearrangement of the intermediate 2-chloroapocamphane-1-acetanilide), and small amounts of PhCN and the lactone (III), m.p. 201.5—202.5°, of 2-hydroxyapocamphane-1-acetic acid. With boiling 20% KOH-EtOH, (I) gives (III) (60% yield) (and NH_2Ph), converted (KOH-KMnO₄) into 2-ketoapocamphane-1-acetic acid (84.4%), m.p. 92—93°, the semicarbazone, m.p. 199—200°, of which with NaOEt-EtOH at 170—180° yields apocamphane-1-acetic acid, m.p. 77—78°. PCl_5 in Et_2O converts (I) into (II). Hydrolysis of (II) by boiling 20% KOH-EtOH gives camphenecarboxylic acid (23.2%), m.p. 126—127° (and NH_2Ph), oxidised by KMnO₄ to camphenilone, which is obtained also directly from (II) by KOH-KMnO₄. R. S. C.

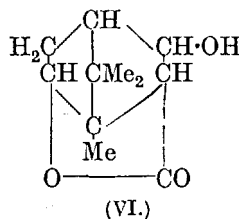
cyclopentadiene series. II. α - and β -Camphylic acids and their decarboxylation products. 1:5:5-Trimethyl- $\Delta^{1:3}$ -cyclopentadiene. K. ALDER and W. WINDEMUTH (Annalen, 1939, **543**, 28—40).—Fusion of sulphocamphylic acid with NaOH at 210—215° gives di- β -camphylic acid (I) (+ AcOH), m.p. 234° (not the α -compound; cf. Perkin, J.C.S., 1903, **83**, 862), and (primarily) β -camphylic acid (II). Thus, distillation of the material after separation of (I), at 12 mm.



affords α -camphylic acid (III) is the sole product; (III) arises by isomerisation of (II). Depolymerisation of (I) by distillation at atm. pressure gives (III), but the Me_2 ester, m.p. 64° (prep. by $\text{Et}_2\text{O}-\text{CH}_2\text{N}_2$), of (I) at 220—230° (bath)/350 mm. affords Me β -camphylate (IV) [the adduct, m.p. 132—133° (see below), of (IV) and $(\text{CH}\cdot\text{CO})_2\text{O}$ (V) is obtained if depolymerisation is effected in C_6H_6 + (V) at 220°]. Distillation of a mixture of the Ca salts of (II) and (III) with soda-lime gives the hydrocarbon, C_8H_{12} (VI), b.p. 133—135°, of Damsky (A., 1888, 293), which is not identical with 1:5:5-trimethyl- $\Delta^{1:3}$ -cyclopentadiene, b.p. 99—105° [structure proved (cf. below) by diene syntheses; obtained by decarboxylation of (II) or (III) with Cu chromite in quinoline and N_2 at 235—240°]. Diene reactions prove that (VI) is a trimethylcyclopentadiene; its formation must involve migration of Me. H. B.

Diene synthesis. XII. Formation of compounds of the camphor and epicamphor group by diene synthesis. Diene syntheses of 1:5:5-trimethyl- $\Delta^{1:3}$ -cyclopentadiene and β -camphylic acid with vinyl acetate. K. ALDER and E. WINDEMUTH (Annalen, 1939, **543**, 41—56).—1:5:5-Trimethyl- $\Delta^{1:3}$ -cyclopentadiene (I) and $\text{CH}_2\text{CH}\cdot\text{OAc}$ (II) at 235—240° give a mixture (A), b.p. 92—94°/12 mm., of dehydrobornyl and dehydroepibornyl acetate (major product); reduction (H_2 , PtO₂, AcOH) and subsequent hydrolysis (20% MeOH-KOH) of (A) affords dl-borneol (III), m.p. 204°, and dl-epiborneol

(IV), m.p. 175—176°, separable through their respective 3:5-dinitrobenzoates, m.p. 154—155° and 105°. Oxidation (CrO_3 , AcOH) of (III) gives dl-camphor [semicarbazone, new m.p. 242° (decomp.; rapid heating)], reduced (Wolff-Kishner) to camphane (V); dl-epicamphor [semicarbazone, m.p. 235° (decomp.)] is similarly obtained from (IV) and reduced to (V). The above reactions prove the structure of (I). The trimethylcyclopentadiene, C_8H_{12} (see above), and (II) at 170—180° afford the acetate, b.p. 203—212°, of a trimethyl-2:5-endomethylene- Δ^3 -cyclohexenol; reduction and subsequent hydrolysis gives the -cyclohexanol, m.p. 98—99° (phenylcarbamate, m.p. 111—112°), oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$, dil. H_2SO_4 , AcOH) to the -cyclohexanone (semicarbazone, m.p. 222°). Me β -camphylate and (II) at 230° give a mixture (B), b.p. 142—146°/12 mm., of Me 4- and 5-acetoxy-6-methyl-3:6-endoisopropylidene- Δ^1 -cyclohexene-1-carboxylate. Successive treatment of (B) with MeOH-HCl (hydrolysis of OAc) and CrO_3 -AcOH (at room temp.) affords the mixed CO-esters, which yield a semicarbazone, m.p. 230—231° (decomp.); this with EtOH-NaOEt at 200—205° gives dl-bornylene-2-carboxylic acid, an oil, oxidised by HNO_3 (d 1.27) to dl-camphoric acid. Hydrolysis (25% MeOH-KOH) of (B) affords a OH-acid, m.p. 159°, a OH-lactone, m.p. 206° [probably (VI); phenylcarbamate, m.p. 177°] [oxidised to a ketone (semicarbazone, m.p. 237°)], and much oily material. H. B.



Diene synthesis. XIII. Diene syntheses of 1:5:5-trimethyl- $\Delta^{1:3}$ -cyclopentadiene and α - and β -camphylic acids with maleic anhydride and acetylenedicarboxylic acid. K. ALDER and E. WINDEMUTH (Annalen, 1939, **543**, 56—78).—1:5:5-Trimethyl- $\Delta^{1:3}$ -cyclopentadiene (I) and $(\text{CH}\cdot\text{CO})_2\text{O}$ in Et_2O give endocis-3-methyl-3:6-endoisopropylidene- Δ^4 -tetrahydrophthalic anhydride, m.p. 137°; the free acid, m.p. 173° (decomp.) [with Br in aq. Na_2CO_3 affords a bromolactonemonocarboxylic acid, $\text{C}_{12}\text{H}_{15}\text{O}_4\text{Br}$, m.p. 208° (Me ester, m.p. 130°), and a little of an ? isomeride, m.p. 215°], is reduced (H_2 , PtO₂, AcOH) to endocis-3-methyl-3:6-endoisopropylidenehexahydrophthalic acid, m.p. 173° (decomp.) (anhydride, m.p. 171°), which is rearranged by boiling MeOH-NaOMe to the trans-acid, m.p. 236—237°. $(\text{CH}\cdot\text{CO})_2\text{O}$ and (I) in Et_2O at 90—100° give Me_2 3-methyl-3:6-endoisopropylidene-3:6-dihydrophthalate, b.p. 142—143°/12 mm., reduced (H_2 , colloidal Pd, MeOH) to the Me_2 ester, b.p. 143—144°/12 mm., of 3-methyl-3:6-endoisopropylidene- Δ^1 -tetrahydrophthalic acid (II), m.p. 172° (anhydride, m.p. 115—116°). The adduct from (I) and $(\text{CH}\cdot\text{CO}_2\text{H})_2$ in Et_2O at 120—130° is reduced (H_2 , colloidal Pd, Na salt in H_2O) to (II), which is oxidised (43% HNO_3 at 120—130°) to dl-camphoric acid. The trimethylcyclopentadiene, C_8H_{12} (III) (see above), and $(\text{CH}\cdot\text{CO})_2\text{O}$ in Et_2O give a trimethyl-3:6-endomethylene- Δ^4 -tetrahydrophthalic anhydride, m.p. 95—96° [free acid, m.p. 158—159°, with Br-aq. Na_2CO_3 affords a bromolactonemonocarboxylic acid,

$C_{12}H_{15}O_4Br$, m.p. 193—194° (decomp.) (*Me* ester, m.p. 133—134°), reduced (H_2 , PtO_2 , $AcOH$) to the *hexahydrophthalic anhydride* (IV), m.p. 185—186°, and oxidised ($KMnO_4$) to a *dilactonic ether*, $C_{12}H_{14}O_5$, m.p. 235—236° (cf. A., 1936, 1250). The adduct, m.p. 175—176°, from (III) and $(:C\cdot CO_2H)_2$ in Et_2O is reduced (Pd; as above) to a *trimethyl-3:6-endo-methylene- Δ^1 -tetrahydrophthalic acid* (V), m.p. 178—179° (*anhydride*, m.p. 61—62°), further reduced (H_2 , PtO_2 , $AcOH$) to (IV) (as acid). The Et_2 ester, b.p. 182—183°/17 mm., of (V) is obtained by reduction (H_2 , colloidal Pd, $MeOH$) of the adduct, b.p. 174—175°/20 mm., from (III) and $(:C\cdot CO_2Et)_2$ at 260—280°.

Me α -camphylate (VI) and $(:CH\cdot CO)_2O$ in boiling C_6H_6 give endocis-6-carbomethoxy-3-methyl-3:6-endoisopropylidene- Δ^4 -tetrahydrophthalic anhydride, m.p. 115° [corresponding acid, m.p. 195°, converted by Br in H_2O into a bromolactonemonocarboxylic acid, $C_{14}H_{17}O_6Br$, m.p. 185° (*Me* ester, m.p. 172°)], reduced (H_2 , PtO_2 , $AcOH$) to the *hexahydrophthalic anhydride*, m.p. 94—95°. $(:C\cdot CO_2Me)_2$ and (VI) in Et_2O at 110—115° afford *Me*₃ 4-methyl-1:4-endoisopropylidene-1:4-dihydrobenzene-1:2:3-tricarboxylate, m.p. 72°, reduced (H_2 , Pd- $CaCO_3$, $EtOH$) to the Δ^2 -tetrahydro-derivative, m.p. 45—46°; this is hydrolysed (20% $MeOH$ - KOH) to a *Me* H_2 ester, m.p. 204°, differing from the isomeric 1-*Me* H_2 ester, m.p. 210° (*anhydride*, m.p. 119°), obtained by reduction (Pd colloid) of the adduct (as Na salt) from (VI) and $(:C\cdot CO_2H)_2$. *Me* β -camphylate and $(:CH\cdot CO)_2O$ in C_6H_6 at 120° give endocis-4-carbomethoxy-3-methyl-3:6-endoisopropylidene- Δ^4 -tetrahydrophthalic anhydride, m.p. 132—133° [corresponding acid, m.p. 165°, whence a non-homogeneous bromolactonic acid, $C_{14}H_{17}O_6Br$, m.p. 219° (decomp.), and material, m.p. 230°], which could not be reduced (H_2 , PtO_2 , $AcOH$) and, like all the Δ^4 -derivatives (above), does not add PhN_3 .

H. B.

Constituents of the herb *Gratiola officinalis*.

I. K. MAURER, K. MEIER, and G. REIFF (Ber., 1939, 72, [B], 1870—1873; cf. Retzlaff, A., 1903, i, 107).—Percolation of *G. officinalis* with Et_2O at room temp., evaporation of the extract to dryness, and extraction of the residue with light petroleum gives gratiolon (I), $C_{30}H_{48}O_3$, m.p. 311—312° (block), $[\alpha]_D^{25} +5.7^\circ$ in C_5H_5N . (I) contains CO_2H since it is converted by CH_3N_2 in Et_2O into the *Me* ester, m.p. 220°, $[\alpha]_D^{25} +5.0^\circ$ in $CHCl_3$, which is hydrolysed with difficulty and hence contains CO_2Me united to *tert. C*. Gratiolon *Me* ester acetate has m.p. 197°. (I) and $NaOAc$ in boiling Ac_2O afford gratiolon acetate, m.p. 268°, $[\alpha]_D^{19} +20.4^\circ$ in $CHCl_3$. (I) contains one double linking since it gives a yellow colour with $C(NO_2)_4$ in $CHCl_3$ and absorbs O from BzO_2H in $CHCl_3$ - $MeOH$. Bromination in $MeOH$ - CCl_4 of (I) affords gratiolonbromolactone (II), $C_{30}H_{47}O_3Br$, m.p. 257°, feebly dextrorotatory in dioxan, which does not give a colour with $C(NO_2)_4$; it is re-converted into (I) by Zn dust in boiling $COMe_2$. The acetate has m.p. 186°, $[\alpha]_D^{25} +12.5^\circ$ in $CHCl_3$. Hydrolysis of (I) gives a halogen-free compound, m.p. 239° (decomp.), which has not been investigated further. (II) is oxidised (CrO_3 in $AcOH$) at room temp. to the *Br*-ketone, m.p. 232° (*oxime*, $C_{30}H_{46}O_3NBr$, m.p. 188°, $[\alpha]_D^{21} -5.5^\circ$ in $CHCl_3$). (I)

appears to be a new member of the triterpene group.
H. W.

Constituents of *Lindera strychnifolia*, Vill., root. III. H. KONDO and K. TAKEDA (J. Pharm. Soc., Japan, 1939, 59, 162—168).—Extraction of the root, best with Et_2O , gives linderan (I) (0.11%), m.p. 187° (decomp.), linderen (II) (0.14%), linderol (= *l*-borneol) (0.1%), esters, b.p. 100—145°/5 mm. (0.46%), and a fraction, b.p. 145—170°/5 mm. (0.37%). The formula of (I) is uncertain; $K_2Cr_2O_7$ and KOH - $EtOH$ give indefinite substances; $Hg(OAc)_2$ (equiv. to 2 H) gives an oily acid and a neutral substance, m.p. 197°; O_3 gives CH_2O and $MeCHO$; H_2 -Pd-C gives 55% of a neutral and 45% of an acidic substance, the latter being the sole product from H_2 - PtO_2 . (I) thus contains a furan ring. (II) is $C_{15}H_{18}O_2$ or $C_{16}H_{20}O_2$, has $[\alpha]_D -15.14^\circ$, gives a maleic anhydride adduct, is stable to KOH - $EtOH$ or CO -reagents and, nearly so, to $Hg(OAc)_2$; O_3 gives CH_2O and two acids; CrO_3 gives an acid, $C_{14}H_{18}O_5$, decomp. 192—195°, and four neutral substances, $C_{15}H_{18}O_4$, m.p. 140°, $C_{15}H_{16}O_4$, m.p. 108°, m.p. $\sim 62^\circ$, and decomp. ~ 195 —200°; dehydrogenation by Pd-asbestos at 250—300° gives an azulene, $C_{15}H_{16}$, +0.66 H_2O , m.p. 105—106° (*picrate*, decomp. 136°; *styphnate*, decomp. 134°); H_2 - PtO_2 gives substances, $C_{15}H_{26}O$, b.p. 130—135°/5 mm., $[\alpha]_D^{23} -53.07^\circ$, and $C_{15}H_{24(26)}O_2$, m.p. 118—119°, $[\alpha]_D^{21.5} -34.78^\circ$ (1 active H; acetate, m.p. 77—79°, prepared by $AcCl$; benzoate, m.p. 169—170°; Ac_2O gives an isomeric alcohol, m.p. 77—79°).

R. S. C.

Colouring matters of *Penicillium carminoviolaceum*, Biourge. Production of ergosterol by the mould. H. G. HIND (Biochem. J., 1940, 34, 67—72).—The mycelium of this mould when grown on an inorg. medium containing glycerol (or carbohydrate) as source of C contains two pigments, carviolin, $C_{16}H_{12}O_6$, m.p. 286° (*triacetate*, m.p. 210°; *Me*₃ ether, m.p. 186°; *tribenzoate*, m.p. 240°; *leuco-carviolin penta-acetate*, m.p. 247°), and carviolacin, $C_{20}H_{16}O_7$, m.p. 243° (decomp.) (*acetate*, m.p. 230°; *Me*₃ ether, m.p. 214—215°), together with ergosterol. The two pigments are both *Me*₁ ethers and are probably complex hydroxyanthraquinones. Distillation of carviolacin with Zn in H_2 yields 2-methylantracene.
J. N. A.

Saponins and sterols. XIII. Ursolic acid. K. FUJII and S. OSUMI (J. Pharm. Soc., 1939, 59, 142—143).— α -Ursolic acid (I), m.p. 284—285°, contains $\sim 10\%$ of *uvaol* (II), $C_{30}H_{50}O_2$, m.p. 233° (*diacetate*, m.p. 157—159°), and, when pure, melts at 291—292° and gives only the *Me* ester (III), m.p. 172°. A 1:1 mixture of (II) and (III) melts sharply at 231—233°, and the substance, m.p. 230°, thought previously to be another *Me* ester of (I), was a mixture of (II) and (III).
R. S. C.

Sterols. LXXX. Reactions of chlorogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 3479—3482).—Chlorogenone is identical with the diketone obtained from diosgenin. Chlorogenin resembles tigogenin more closely than it does sarsasapogenin. It is unchanged by HCl - $EtOH$ or Zn - Hg - $EtOH$ - HCl . Hydrogenation (PtO_2)

in AcOH at 70°/3 atm. gives *dihydrochlorogenin*, m.p. 233—235° (*tri-3:5-dinitrobenzoate*, m.p. 210—212°), stable to Br or SeO₂, oxidised by CrO₃-AcOH at room temp. to (?) 3:6-*dehydroanhydrotetrahydrochlorogenoic acid*, C₂₂H₄₀O₅, m.p. 202—204° [*disemicarbazone*, m.p. 240° (decomp.)]; Me₁ ester, m.p. 156·5—158°. Chlorogenin diacetate with Br and a trace of HBr in AcOH gives *bromochlorogenin diacetate*, m.p. 200° (slight decomp.), and with CrO₃-AcOH at 90—95° gives chlorogenin lactone diacetate, m.p. 247—250°, and thence chlorogenin lactone, C₂₂H₃₄O₄, m.p. 250—251·5° (*dibenzoate*, m.p. 278—280°), further oxidised at 25° to a *diketo-lactone*, C₂₂H₃₀O₄, m.p. 243—245°. Deoxychlorogenin and H₂-PtO₂ in AcOH at 25°/3 atm. give dihydrodeoxytigogenin.

R. S. C.

Sterols. LXXXV. Oxidation of sarsasapogenin acetate with potassium permanganate. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, **62**, 222—223).—KMnO₄ oxidises sarsasapogenin acetate in aq. AcOH at 20° or 50—70° to products, which by hydrolysis yield sarsasapogenin lactone, the CO-acid, C₂₂H₃₄O₂, and sarsasapogenoic acid. No oxidation occurs in Na₂CO₃-aq. C₅H₅N at 70° or in boiling C₅H₅N. Sarsasapogenin lactone acetate is stable to KMnO₄ in aq. AcOH. Oxidation thus probably occurs by two independent routes.

R. S. C.

Constituents of resins. XIV. Crystalline constituents of *Cryptomeria* resin. II. G. FUKUI and T. CHIKAMORI (J. Pharm. Soc. Japan, 1939, **59**, 158—162).—Substance A (*ibid.*, 1937, **57**, 92) is a phenolic ketone (I), C₂₀H₂₈O₂, m.p. 283—284° (decomp.), $[\alpha]_D^{25} + 34\cdot3^\circ$ in C₅H₅N {Me ether (II), m.p. 137°, $[\alpha]_D^{25} + 31\cdot4^\circ$ [oxime, decomp. 166° (acetate, m.p. 106—107°); (N·OH)₂-derivative, decomp. 180°; semicarbazone, decomp. 254°]; benzoate, m.p. 186°, $[\alpha]_D^{25} + 29\cdot6^\circ$; acetate, m.p. 165°, $[\alpha]_D^{25} + 26\cdot7^\circ$; oxime, decomp. 176·5°; semicarbazone, decomp. 246°}, sol. in 5% NaOH. Clemmensen or Wolff-Kishner reduction of (II) gives an oil, b.p. 165—170°/0·5 mm., dehydrogenated by Se at 280—320° to (? 8-) methoxyretene (III). Hinokiol and (I) have an absorption max. at 3500 Å. and are isomeric cyclic ketones; both substances and (II) give the CHI₃ reaction, but this is due to the Pr⁸.

R. S. C.

Constituents of *Didymocarpus pedicellata*. IV. Isolation of two new colouring matters and their relationship to pedicin. S. WARSI and S. SIDDIQUI (J. Indian Chem. Soc., 1939, **16**, 519—524).—Extraction of *D. pedicellata* leaves with ligroin and Et₂O yields *ψ-isopedicin*, C₁₈H₁₈O₆, m.p. 126°, also obtained from pedicin and HCl in EtOH or from isopedicin on keeping. *Pedicin*, C₃₇H₃₆O₁₁, m.p. 190° was also obtained and this with HNO₃ in AcOH gives a substance, m.p. 164—166°.

F. R. G.

Lignin. XXV. Model experiments on the lignin question. K. FREUDENBERG, H. RICHTZENHAIN, E. FLICKINGER, and K. ENGLER (Ber., 1939, **72**, [B], 1805—1809).—The view is expressed that the main bulk of pine lignin (24% out of 27% present in wood) is pre-formed in the wood by physiological union and condensation from phenylpropane units and exists as a product of high mol. wt.; only

a small proportion can be present in a simple form. At least 90% of pine lignin is immediately insol. in alkali and org. media, does not contain phenolic OH, and gives veratric (I) and isocheminipinic (II) acid when treated with alkali and then methylated and oxidised. The formation of (II) is most characteristic of pine lignin. α-Ethoxypropiovanillone is scarcely affected by the treatment used in preparing lignin by the cuproxam process. The corresponding carbinol gives a brown amorphous product resembling lignin in appearance but sol. in alkali and in org. media; after methylation it affords (I) but not (II). Coniferaldehyde or the corresponding ethylene oxide (as glucoside) behaves similarly. The bulk of the lignin is therefore pre-formed in the wood and not produced by chemical reagents during its isolation or by post-mortem ageing in the wood.

H. W.

Lignin. XXVI. Stilbene derivative from sulphite liquor. H. RICHTZENHAIN and C. VON HOFFE (Ber., 1939, **72**, [B], 1890—1892).—Treatment of pine wood sulphite liquor with alkali under pressure gives 4:4'-dihydroxy-3:3'-dimethoxystilbene (I) m.p. 212—213°. The yield varies greatly and under the most favourable conditions attains 1% of the lignin; in other cases only traces are formed. Since (I) is not present before the treatment with alkali it is assumed to be formed during this treatment from some component of the liquor which, however, is not vanillin simultaneously produced. (I) is converted by NaOH-Me₂SO₄ into 3:3':4:4'-tetramethoxystilbene (II), m.p. 153°, and by C₅H₅N-Ac₂O into 4:4'-diacetoxy-3:3'-dimethoxystilbene, m.p. 226°; this is reduced (Pd-BaSO₄ in AcOH) to 4:4'-diacetoxy-3:3'-dimethoxydibenzyl, m.p. 140—141°, which is hydrolysed to 4:4'-dihydroxy-3:3'-dimethoxydibenzyl, m.p. 158°. Syntheses of (I) from tris-thiovanillin and of (II) from thioveratraldehyde are recorded. Oxidation (KMnO₄ in aq. COMe₂) of (II) yields veratric acid.

H. W.

Enzymic degradation of polymeric hydrocarbons. III. Behaviour of lime wood toward ethylenediamine-copper oxide solution and enzymic degradation of the main fractions. T. PLOETZ (Ber., 1939, **72**, [B], 1885—1889).—Treatment of the wood (I) of *Tilia tomentosa*, which has been extracted with EtOH-C₆H₆, with (CH₂NH₂)₂-Cu(OH)₂ gives a residue (II) (61%). Acidification of the extract gives 12·7% as ppt. (III). (I) and (II) have almost the same elementary composition but (I) contains cellulose 45·5%, pentoses 26·1%, and lignin 18% whereas the corresponding data for (II) are 60·5, 8·67, and 20·53%. Lignins obtained from (I) and (II) differ in composition (III) is a yellow, non-homogeneous powder which gives 26·14% of lignin with H₂SO₄. (III) consists of lignin and a methoxylated compound which does not pass into Klason's lignin. (II) and (III) are free from N. (I) is very resistant to an enzyme prep. from *Helix pomatia* containing cellulase, lichenase, and cellobiase; after 8 days only 14% has been dissolved and 35% of the sugars consists of pentoses. (II) is likewise very resistant and after very protracted action only 18·6% of the material passes into solution; this comprises the whole of the pentoses contained in (II).

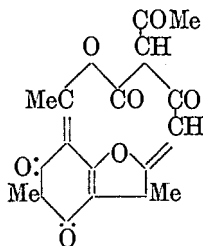
(III) is relatively easily degraded. Pentoses constitute 70% of the dissolved sugar. H. W.

Constituents of derris root. III. T. M. MEIJER (Rec. trav. chim., 1939, **58**, 1119—1123; cf. A., 1939, II, 484).—Derride and KOH-EtOH give 3-hydroxy-coumarone-4-carboxylic acid, m.p. 214° (decomp.). Derridenone and H₂O₂-aq. KOH give furan-2:3-dicarboxylic acid, m.p. 224—225° (decomp.), and a substance, m.p. 151—152°. Dehydoderride and KMnO₄-COMe₂ give rissic acid and 2:4:5:1-OH·C₆H₃(OMe)₂·CO₂H. A. T. P.

Reaction between quinones and metallic enolates. X. Trimethyl[benzo]quinone and enolates of β-diketones. XI. Duroquinone and the enolates of cyanoacetic ester and of β-diketones. L. I. SMITH and E. W. KAISER (J. Amer. Chem. Soc., 1940, **62**, 133—138, 138—140).—X. Addition of trimethyl-*p*-benzoquinone (I) in EtOH to CH₂Ac₂ and NaOEt-EtOH at 0°—room temp. gives a 72% yield of γ-3:6-dihydroxy-2:4:5-trimethylphenylacetylacetone (II), m.p. 129—130° [with NHPH·NH₂ gives a product, m.p. 205—206° (decomp.)], converted by HCl-EtOH into 4-hydroxy-1:3:5:6-tetramethylcoumarone (III), m.p. 138—139° (acetate, m.p. 91—92°). Ac₂O and a drop of H₂SO₄ at room temp. convert (II) exothermally into a mixture consisting mainly of 3:6-diacetoxy-2:4:5-trimethylphenylacetone, m.p. 135.5—136° [oxime, m.p. 172—175° (decomp.)], cyclised by hot HCl or by NaOH at room temp. to (III). Addition of (II) to (Pr²CO)₂O-H₂SO₄ (trace) (room temp.) or (CH₂Cl·CO)₂O (45—50°) causes acylation of the 3-OH and migration of an Ac from the diketone portion of the mol. to the neighbouring 6-OH; the products are thus 6-acetoxy-3-isobutyroxy-, m.p. 127.5—128°, and -3-chloroacetoxy-, m.p. 162—163°, -2:4:5-trimethylphenylacetone, respectively; the migration occurs by intermediate formation of a 1-hydroxydihydrobenzofuran. COMe·CH₂·COPr², (I), and NaOEt-EtOH give γ-3:6-dihydroxy-2:4:5-trimethylphenyl-ε-methyl-n-hexane-βδ-dione (81%), m.p. 131.5—132.5° [with NHPH·NH₂ gives a product, m.p. 167° (decomp.)], converted by Ac₂O and a drop of H₂SO₄ into a mixture containing 3-acetoxy-6-isobutyroxy-2:4:5-trimethylphenylacetone, m.p. 114—115.5° [oxime, m.p. 165—170° (decomp.)], by hot, conc. HCl into (III), and by hot, conc. HCl-EtOH into (probably) a mixture of (III) and 4-hydroxy-3:5:6-trimethyl-1-isopropylcoumarone. With CH₂Ac·COPr², (I) gives (NaOEt-EtOH) an oil, with COMe·CH₂·COPh gives a trace of a solid, m.p. 110—120°, and does not react with CH₂Bz₂. Under certain conditions, (I) and CHNaAc·CO₂Et in EtOH give 4-hydroxy-2-acetyl-3:5:6-trimethylcoumaranone, m.p. 126.5—128° (gives no ether or oxime), converted by distillation in steam into (III) and 4-hydroxy-3:5:6-trimethylcoumaranone (cf. A., 1936, 732).

XI. The driving force in the formation of heterocyclic O compounds from duroquinone (IV) and ester enolates is elimination of EtOH in the ring-closure. The earlier stages postulated are reversible and attempts to add CH₂Ac₂ under various conditions failed. The Na derivative of CN·CH₂·CO₂Me and (IV) in boiling C₆H₆ (7 days) give 6-hydroxy-3-cyano-5:7:8-

trimethylcoumarin, m.p. 261.5—263° (acetate, m.p. 227—228°), stable to H₂O₂ but hydrolysed by 81% H₂SO₄ at 100° to 6-hydroxy-3-carbamyl-5:7:8-trimethylcoumarin, m.p. 288—290° (decomp.; tube), 302° (decomp.; block) (? Ac₂ derivative, m.p. 243—244.5°), resistant to further hydrolysis, the structure of which is proved by synthesis from the corresponding acid by way of the acid chloride. R. S. C.



Constitution of usnic acid. Y. ASAHINA (Proc. Imp. Acad. Tokyo, 1939, **15**, 311—314).—The reactions and degradations of usnic acid and its derivatives are discussed, and the annexed structure is proposed as most fully explaining the known properties of usnic acid. J. D. R.

Syntheses of chroman derivatives with the ring system of α-tocopherol. II. W. JOHN and P. GUNTHER. III. Introduction of a side-chain into hydroxytetramethylchroman. W. JOHN and M. SCHMEL (Ber., 1939, **72**, [B], 1649—1653, 1653—1656).—II. Trimethylquinol (I) is converted into 3:6-dimethoxy-2:4:5-trimethylbenzaldehyde, which with aq. NaOH and 70% COMe₂ at 15—20° yields 3:6-dimethoxy-2:4:5-trimethylbenzylideneacetone (II), m.p. 61—62°, with some tetramethoxyhexamethyldibenzylideneacetone, m.p. 188°. (I) is hydrogenated (Pd sponge in EtOH) to 3:6-dimethoxy-2:4:5-trimethylbenzylacetone (III), m.p. 76°, which when treated successively with MgMeI in Et₂O and HBr (*d* 1.49) in boiling AcOH yields 6-hydroxy-2:2:5:7:8-pentamethylchroman, m.p. 93—94°. The process appears unsuitable for the introduction of long side-chains at C₍₂₎. Mg dodecyl bromide and (III) readily give the corresponding carbinol, with which ring-closure could not be achieved satisfactorily by HBr or HI in AcOH, AlCl₃, or AlBr₃ in C₆H₆, or by KI, red P, and H₃PO₄. HBr in boiling AcOH de-etherifies (III) but reduction occurs simultaneously with production of 6-hydroxy-2:5:7:8-tetramethylchroman, m.p. 145°. (I) is transformed by Et₂SO₄ and NaOH in EtOH into the Et₂ ether, m.p. 34° (etherification with EtI gives a halogenated material, m.p. 82°), which is converted into 3:6-diethoxy-2:4:5-trimethylbenzaldehyde, m.p. 100.5°; the dihydroxy-, m.p. 149°, and monohydroxymonoethoxy-, m.p. 99°, -aldehydes are formed as by-products.

III. 6-Hydroxy-2:5:7:8-tetramethylchroman is oxidised by FeCl₃ or, preferably, by AgOAc in boiling MeOH to 3:4:6-trimethyl-1-γ-hydroxybutyl-*p*-benzoquinone, m.p. 79°, which is reduced by alkaline Na₂S₂O₄ to the corresponding quinol, m.p. 138°, and is oxidised by CrO₃ in AcOH at room temp.—30° to 3:4:6-trimethyl-1-γ-ketobutyl-*p*-benzoquinone (IV), m.p. 56°. This is converted by Zn dust in AcOH at 100° into 3:4:6-trimethyl-1-γ-ketobutylquinol, m.p. 122°, or by reductive acetylation into the corresponding diacetate (V), m.p. 94°. The corresponding dibenzoate (VI), m.p. 93°, is almost quantitatively oxidised by CrO₃ in AcOH at 30° to the benzoate, m.p. 143°, of (IV). Gradual addition of (IV) in Et₂O to a boiling solution of MgMeI in Et₂O affords 6-hydroxy-2:2:5:7:8-pentamethylchroman, m.p. 93°. Analo-

gously Mg dodecyl bromide gives 6-hydroxy-2:5:7:8-tetramethyl-2-dodecylchroman, isolated as the allophanate, m.p. 180°. The Grignard compounds and (V) or (VI) give very sparingly sol., additive compounds which have not been investigated. H. W.

Vitamin-E. XXI. Dealkylation of hydroquinone ethers related to the tocopherols. L. I. SMITH, H. E. UNGNADE, and W. B. IRWIN. **XXII. Reaction between Grignard reagents and coumarins and hydrocoumarins.** L. I. SMITH and P. M. RUOFF (J. Amer. Chem. Soc., 1940, **62**, 142—144, 145—148).—XXI. 3:6:2:4:5:1-

(OMe)₂C₆Me₃[CH₂]₂·COMe and MgMeI in Et₂O give β-3:6-dimethoxy-2:4:5-trimethylphenylethyl-dimethylcarbinol (I), an oil [3:5-dinitrobenzoate (II), m.p. 148—148.5°], demethylated by treatment with MgMeI-Et₂O and subsequent heating at 180° to the 3:6-(OH)₂-compound, which is reversibly oxidised by air to the *p*-quinone (III) and gives an oily triacetate, converted by hot HNO₃-EtOH into the red chroman-*o*-quinone. 6-Hydroxy-2:2:5:7:8-pentamethylchroman and AgOAc-MeOH give the quinone (III), an oil (lit. m.p. 62°), which by cautious reductive methylation yields (I), identified as (II).

XXII. When treated with MgEtBr in Et₂O, coumarin suffers ring-fission, giving α-*o*-hydroxyphenyl-γ-ethyl-Δ^a-*n*-pentan-γ-ol, m.p. 67—68°, which with H₂-PtO₂ in EtOH gives the saturated alcohol (also obtained from dihydrocoumarin by MgEtBr) and, when boiled in AcOH and distilled, gives 2:2-diethyl-Δ³-chromene, b.p. 125—126°/14 mm., and other products. α-*o*-Hydroxyphenyl-γ-methyl-Δ^a-*n*-butan-γ-ol (prep. from coumarin), m.p. 53—55°, α-*o*-hydroxyphenyl-γ-*n*-butyl-*n*-heptan-γ-ol (prep. from dihydrocoumarin), m.p. 67—68.5°, 2:2-dimethyl-, b.p. 96—97°/15 mm., and 2:2-di-*n*-butyl-Δ³-chromene, b.p. 164—165°/15 mm., and 2:2-di-*n*-butylchroman, b.p. 165—168°/8 mm., are similarly prepared.

R. S. C.

Structure of the red oxidation products of tocopherols and related substances. L. I. SMITH, W. B. IRWIN, and H. E. UNGNADE (Science, 1939, **90**, 334—335).—The red cryst. compound, m.p. 109—110°, obtained by the action of AgNO₃ or HNO₃ on 6-hydroxy-2:2:5:7:8-pentamethylchroman, is CMe₂CMe₂C(O)CMe₂CO₂ (I), i.e., an *o*- and not a *p*-quinone. *o*-C₆H₄(NH₂)₂ and (I) give a phenazine, m.p. 151—152°. The condensation products of *o*-xyloquinol and isoprene give (I) with AgNO₃ or HNO₃. The red *o*-quinone, and its phenazine, from α-tocopherol are oils. 5-Hydroxycoumarins and related substances and *o*-C₆H₄(OH)₂ form red *o*-quinones in the Furter-Meyer reaction (A., 1939, III, 404).

L. S. T.

Geometrical inversion in the acids derived from the coumarins. VII. Behaviour of acetylcoumaric acids. P. S. RAO, V. D. N. SASTRI, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, **10**, A, 267—274).—Acetylcoumaric acid (I), m.p. 154—155°, is best obtained by treating coumaric acid with Ac₂O and anhyd. NaOAc at 100°; at higher temp. the yields are less. Similarly prepared are acetyl-4-methyl- (II), m.p. 155°, and acetyl-5-nitro- (III),

m.p. 217°, -coumaric acid, acetylpsoralic (IV), m.p. 180—181°, and acetylisopsoralic acid (V), m.p. 210—211°. (I) is little affected by exposure to sunlight for 48 hr. but is completely transformed after 200 hr. into coumarin (VI). With (II) 80—85% inversion is produced in 200 hr. (III) gives 5% of 6-nitrocoumarin after 24 hr. and undergoes complete conversion after 200 hr. (IV) and (V) do not afford psoralene or isopsoralene after 24 hr. In all experiments small amounts of amorphous, sparingly sol., complex products are formed probably owing to polymerisation. (I) is transformed at ~200° into (VI), CO₂, AcOH, and resinous matter from which a definite compound could not be isolated. At 210° (II) behaves similarly. At 255° (III) affords 6-nitrocoumarin in 75% yield. (IV) and (V) at 230° and 240° suffer ~75% and ~80% conversion, respectively. (I) is transformed by HgCl₂ in boiling EtOH or H₂O into coumarin Hg^{II} chloride, m.p. 164°, converted by boiling dil. HCl into (VI). When similarly treated (II), (III), (IV), and (V) afford the corresponding coumarins in nearly theoretical yield.

H. W.

Condensation of chalcones with flavanones.

B. N. KAPLASH, R. C. SHAW, and T. S. WHEELER (Current Sci., 1939, **8**, 512).—Ph styryl ketone, 2-phenyl-2:3-dihydro-1:4-benzopyrone, and 30% NaOH or NaNH₂ or Na give 2-phenyl-3-phenacylbenzyl-2:3-dihydro-1:4-benzopyrone. J. L. D.

Demethylation of wogonin. S. HATTORI (Ber., 1939, **72**, [B], 1914—1917; cf. A., 1931, 493; Shah *et al.*, A., 1938, II, 334).—When wogonin (I) (5:7-dihydroxy-8-methoxyflavone) is heated for > 5 min. with gently boiling HI (*d* 1.7; 15—20 parts) or at 130—135° for 30 min. the main product is 5:7:8-trihydroxyflavone (II). This is also obtained by short, gentle boiling of (I) with Ac₂O-HI (*d* 1.7). If (I) is heated at 145—150° or 150—155° with HI (*d* 1.7)-Ac₂O in the same ratio the product is 5:6:7-trihydroxyflavone (III). HI alone behaves similarly but attempts to isomerise (II) to (III) by boiling HI with or without Ac₂O were unsuccessful. Under mild conditions demethylation is possible without ring-fission and subsequent re-formation of the pyrone ring in a reverse direction.

H. W.

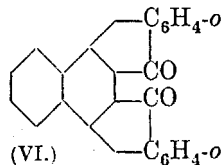
Orobol. C. CHARAUX and J. RABATÉ (Bull. Soc. Chim. biol., 1939, **21**, 1330—1333).—Orobol is 5:7:3':4'-tetrahydroxyisoflavone since boiling aq. 30% KOH gives phloroglucinol and α-homoprotocatechuic acid. P. G. M.

Preparation of substituted xanthenes. A. LESPAGNOL, J. BERTRAND, and J. DUPAS (Bull. Soc. chim., 1939, [v], **6**, 1625—1629).—*o*-OH·C₆H₄·CO₂H or *o*-cresotic acid and thymol-Ac₂O afford xanthone or 1:5-dimethylxanthone, m.p. 165° (1:4:1':4'-tetramethyldixanthylcarbamide), respectively, and not 1-methyl- and 1:5-dimethyl-4-isopropylxanthene (*loc. cit.*). Thymol and *o*-C₆H₄Cl·CO₂H-MeOH at 100° (bath), then with Cu at 150°, then 200°, give thymylsalicylic acid, m.p. 98°, converted by H₂SO₄ at 100° (bath) into 1-methyl-4-isopropylxanthone, m.p. 89°; reduction (Na-Hg) gives the xanthhydrol, m.p. ~85°, converted into 1:1'-dimethyl-4:4'-diisopropyldixanthylcarbamide, m.p. 243°. A. T. P.

Attempted synthesis of morphenol. A. BURGER and S. AVAKIAN (J. Amer. Chem. Soc., 1940, **62**, 226—227).—1-Methoxydibenzfuran-4-carboxylic acid and SOCl_2 give the *acid chloride*, m.p. 162.5—163.5°, and thence 1-methoxy-4-dibenzfuryl CHN_2 ketone, m.p. 150—151° (decomp.), (aq. NH_3 -dioxan), 1-methoxy-4-dibenzfuryl-acetamide, m.p. 203°, and -acetic acid (I), m.p. 223—224°. Attempted ring-closure of (I) to morphenol by various reagents failed. R. S. C.

Fission of heterocyclic compounds of coal tar. O. KRUBER (Ber., 1939, **72**, [B], 1878).—The statement of Weissgerber and Seidler (A., 1927, 1198) that diphenylene oxide is stable to KOH at 300° is erroneous. H. W.

Synthesis of 1:2-diphenyldihydroisobenzfurans, 1:2-diphenylisobenzfurans, and o-dibenzoylbenzene derivatives from the diene addition products to dibenzoylbenzene. R. ADAMS and M. H. GOLD (J. Amer. Chem. Soc., 1940, **62**, 56—61).—The reactions described below render readily accessible by novel methods $\text{o-C}_6\text{H}_4(\text{COAr})_2$, a variety of 1:2-diaryl isobenzfurans and their H_2 -derivatives, and various C_{10}H_8 derivatives. *trans*- or *cis*-(CHBz)₂ and ($\text{CH}:\text{CHMe}$)₂ in boiling, abs. EtOH give 4:5-dibenzoyl-1:2-dimethyl- Δ^1 -cyclohexene (I), m.p. 111—111.5° [dibromide, m.p. 170—171° (decomp.); 2:4-dinitrophenylhydrazones, m.p. 226—228° (decomp.)], and a little 1:2-diphenyl-4:5-dimethyl-3:6-dihydroisobenzfuran (II), m.p. 225—226°, fluorescent in solution, obtained in 99% yield from (I) by a little syrupy H_3PO_4 in boiling Ac_2O . Br and NaOAc in AcOH convert (II) into 4:5-dibenzoyl-o-xylene (III), m.p. 143—144°, oxidised by alkaline KMnO_4 in aq. $\text{C}_5\text{H}_5\text{N}$ to 4:5-dibenzoyl-o-toluic acid, m.p. 196—197°. 1:2-Diphenyl-4:5-dimethylisobenzfuran (IV), m.p. 187—188°, is obtained in 97% yield from (III) by Zn dust (activated by dil. HCl) in NaOH-95% EtOH or, less well, by converting (II) into 4:5-dibromo-1:2-diphenyl-4:5-dimethyl-3:4:5:6-tetrahydroisobenzfuran, m.p. 155—156° (decomp.), by $\text{Br}-\text{CHCl}_3$ and boiling this with NaOAc in $\text{Ac}_2\text{O}-\text{AcOH}$. ($\text{CH}:\text{CO}$)₂ (V) and (IV) in C_6H_6 give 1:4-oxido-1:4-diphenyl-6:7-dimethyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride, m.p. 254—255° (decomp.; sealed tube), converted by boiling with HCl-MeOH and subsequently NaOH-EtOH into 1:4-diphenyl-6:7-dimethylnaphthalene-2:3-dicarboxylic anhydride, m.p. 324—325°, which with cone. H_2SO_4 at room temp. gives 1:2:3:4-dibenzoylene-6:7-dimethylnaphthalene (VI), m.p. >325°. Addition of (V) to (II) is reversible and no product could be isolated. By similar reactions, *trans*-(CHBz)₂ and ($\text{CH}:\text{CH}_2$)₂ (condensed in C_6H_6 at 100°) give 4:5-dibenzoyl- Δ^1 -cyclohexene, m.p. 111.5—112° (dibromide, m.p. 148—149°), 1:2-diphenyl-3:6-dihydroisobenzfuran, m.p. 120—121°, 4:5-dibromo-1:2-diphenyl-3:4:5:6-tetrahydroisobenzfuran, m.p. 150—151° (decomp.), unstable, $\text{o-C}_6\text{H}_4(\text{COPh})_2$, m.p. 145—146° (lit. 145° to 149°), and 1:2-diphenylisobenzfuran, m.p. 125—126° (lit. 125°, 120—125°); addition of (V) to the furans of this series gives unstable products. cyclopentadiene and



trans-(CHBz)₂ in C_6H_6 give 4:5-dibenzoyl-3:6-endo-methylene- Δ^1 -cyclohexene, m.p. 78—79°, in which the Bz are *trans*; *cis*-(CHBz)₂ gives an isomeric adduct, m.p. 160—161°; neither product yields a furan. M.p. are corr. R. S. C.

Azetidine derivatives. I. 3-Hydroxy-2:4-diketo-3-arylazetidines. J. L. RIEBSOMER, H. BURKETT, T. HODGSON, and F. SENOUR (J. Amer. Chem. Soc., 1939, **61**, 3491—3493).— $\text{OH}\cdot\text{C}(\text{Ar})(\text{CO}_2\text{Et})_2$ with $\text{NaOEt}-\text{CO}(\text{NH}_2)_2$ or NH_3 in EtOH at 115—120° gives 6—38% of 3-hydroxy-2:4-diketo-3-phenyl-, m.p. 107.5—108°, -*p*-tolyl-, m.p. 131°, -*p*-ethylphenyl-, m.p. 105—106°, -2:5-dimethylphenyl-, m.p. 135—136°, -*mesityl*-, m.p. 151—152°, and -*p*-sec-butylphenyl-, m.p. 89—90°, -azetidine [*trimethyleneimine*] (cf. A., 1938, II, 278), which have no hypnotic activity (rabbits) but are rather toxic. Structures are proved by hydrolysis (20% NaOH; gives NH_3) and decarboxylation (HCl) to the appropriate $\text{OH}\cdot\text{CHAr}\cdot\text{CO}_2\text{H}$. R. S. C.

Preparation of amines. E. J. SCHWÖGLER and H. ADKINS (J. Amer. Chem. Soc., 1939, **61**, 3499—3502).—Favourable conditions are detailed for condensing ROH (R = Et, Pr^a, Pr^b, Bu^a, *n*-C₆H₁₃, cyclohexyl, CMeEtBu^a, and *n*-C₁₂H₃₅) with *n*-C₅H₁₁NH₂, piperidine, Ph[CH₂]₂NH₂, and/or CHMeBu^bNH₂. By hydrogenating (Raney Ni) mixtures of the appropriate aldehyde or ketone with liquid NH₃ in MeOH at, usually, 150°/150 atm. are obtained CHMeBu^bNH₂ 65, CHPhMeNH₂ 64, CHPh₂NH₂ 19, CHMeBu^aNH₂ 51, CHBu^a₂NH₂ 72, CHPr^b₂NH₂ 48, CH₂PhNH₂ 48, *n*-C₇H₁₅NH₂ 59, and furfurylamine 60%. (CH₂·COMe)₂ gives 59% of 2:5-dimethylpyrrole and 28% of 2:5-dimethylpyrrolidine, b.p. 113—118° (hydrochloride, m.p. 201—202°), but CH₂Ac₂ gives quantitatively NH₂Ac. Formation of *sec.* amines during hydrogenation of nitriles is suppressed by excess of NH₃. Thus, hydrogenation (Raney Ni) of Bu^aCN and *n*-C₆H₁₃CN (0.4—0.7 mol.) in liquid NH₃ (0.9—1.6 mol.) at 125° gives 90—95% of primary and <5% of *sec.* amine. The following are described, m.p. in parentheses being those of the hydrochlorides. 1-β-Ethyl-*n*-hexylpiperidine, b.p. 141°/42 mm. (162—163°). β-Phenyl-ethyl-*n*-, b.p. 102°/16 mm. (218°), and -*iso*-propyl-, b.p. 112°/21 mm. (163—164°), -ethyl-, b.p. 85°/8 mm., and -*n*-butylamine, b.p. 113.5°/6 mm. N-Ethyl-, b.p. 136° (195°), N-*n*-, b.p. 155° [247° (decomp.)], and N-*iso*-propyl-, b.p. 146° (167—167.5°), and N-cyclohexyl-, b.p. 118°/30 mm. (phenylurethane, m.p. 110°), *n*-amylamine. γ-Ethyl-, b.p. 136° (144—145°), -*n*-, b.p. 162° (139°), and -*iso*-propyl-, b.p. 146° (158.5°), -*n*-butyl-, b.p. 179° (149—150°), -dodecyl-, b.p. 170—172°/12 mm. (124.5—125°), and cyclohexyl-, b.p. 106°/21 mm. (198—199°), -aminoisohexane. γ-Aminoisohexane, b.p. 108—109° (139.5°). γ-Amino-β₈-, b.p. 129° (196°), and -β₈-dimethyl-n-pentane, b.p. 102° [296—297° (sublimes)]. 1-*iso*-Propylpiperidine picrate, m.p. 153°. R. S. C.

Aliphatic polyamines. IX. J. VAN ALPHEN (Rec. trav. chim., 1939, **58**, 1105—1108; cf. A., 1937, II, 520).—Br[CH₂]₄·Br and (CH₂·NH₂)₃·H₂O give 1-β-aminoethylpyrrolidine (I), b.p. 166—167° [picrate, decomp. 219°; phenyl-carbamyl (picrate, m.p. 193°)

and *-thiocarbamyl* derivative, m.p. 95°. Its *CHPh*: derivative, b.p. 176°/17 mm., and Na-EtOH give 1- β -benzylaminoethylpyrrolidine, b.p. 172°/20 mm. (*picrate*, m.p. \sim 147°; *phenylthiocarbamyl* derivative, m.p. 133°). A. T. P.

Oxidative fission of the polyhydroxy side-chains in the sugar condensation products of ethyl acetoacetate and *o*-phenylenediamine. A. MÜLLER and I. VARGA (Ber., 1939, 72, [B], 1993—1999).—*d*-Mannose, finely-divided ZnCl_2 , $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and EtOH at 100° rapidly yield *Et* 2-methyl-5-*d*-arabotetrahydroxybutylfuran-3-carboxylate (I), m.p. 147°, $[\alpha]_D^{24}$ -17.9° in MeOH (A_{41} , m.p. 84°, and B_{24} , m.p. 107—110°, $[\alpha]_D^{24}$ -9.5° in CHCl_3 , derivatives), which does not reduce hot Fehling's solution but immediately decolorises Br in H_2O or CHCl_3 or neutral KMnO_4 . It is not obtained when *d*-fructose is used; *d*-galactose does not condense in this direction. Oxidation of (I) by $\text{Pb}(\text{OAc})_4$ in $\text{AcOH}\cdot\text{C}_6\text{H}_6$ yields $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$, *d*-glyceraldehyde, and *Et* 5-aldehydo-2-methylfuran-3-carboxylate (II), m.p. 56°, $[\alpha]_D \pm 0^\circ$ (additive compound with NaHSO_3 ; *phenylhydrazone*, m.p. 100°; *semicarbazone*, m.p. 223°; *dimedon* compound, m.p. 183—184°). (II) is oxidised and hydrolysed by Ag_2O and NaOH in boiling H_2O to 2-methylfuran-3:5-dicarboxylic acid, m.p. 272—274°, decarboxylated above its m.p. to 2-methylfuran-3-carboxylic acid. *Et* 2-methyl-5-*d*-arabotetrahydroxybutylpyrrole-3-carboxylate, m.p. 148—150°, $[\alpha]_D^{24}$ -24.1° in MeOH, from glucosamine hydrochloride, Na_2CO_3 , and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in aq. CMe_2 , is oxidised by $\text{Pb}(\text{OAc})_4$ in C_6H_6 finally at $\sim 35^\circ$ to *Et* 5-aldehydo-2-methylpyrrole-3-carboxylate, m.p. 132—133° $[\alpha]_D \pm 0^\circ$ (*semicarbazone*, m.p. 251°). 2-*d*-arabotetrahydroxybutylquinoxaline is similarly oxidised to quinoxaline-2-aldehyde, m.p. 108° (*phenylhydrazone*, m.p. 231°; *semicarbazone*, m.p. 251°), oxidised to quinoxaline-2-carboxylic acid, m.p. 212° (decomp.). H. W.

Syntheses of pyridiniummethanols. III. Further observations. Physiological action of pyridiniummethanols. F. KRÖHNKE [with A. SCHULZE] (Ber., 1939, 72, [B], 2000—2009; cf. A., 1935, 1131).—Benzylpyridinium bromide and furfuraldehyde in EtOH containing NaOH at 0° give β -hydroxy- α -phenyl- β -2-furylethylpyridinium bromide, m.p. 201—202° (decomp.) (corresponding *perchlorate*, m.p. 108—109°), which becomes successively yellow, greenish-brown, and dark green in conc. HBr and affords a dark brown "picryl chloride reaction." β -Hydroxy- β -2-furylethylpyridinium bromide, m.p. between 183° and 215° greatly dependent on the mode of heating, and the corresponding *perchlorate*, m.p. 151—152°, are obtained similarly. Enolbetaines condense with aldehydes in the absence of alkali. Phenacylpyridinium bromide (I) and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ give an additive compound (1:2), m.p. $<130^\circ$, which separates into its components when shaken with H_2O and Et_2O . The corresponding compound (1:2) from phenacylpyridinium chloride and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is formed only in the presence of NEt_3 , which also facilitates the formation of β -hydroxy- β -*m*-nitrophenylethylpyridinium bromide from its components. The yield of β -hydroxy- β -*m*-hydroxyphenylethylpyridin-

ium bromide, m.p. 268°, from its components is greatly increased by the addition of NaBr. β -Hydroxy- β -phenylethyl- α -vinylpyridinium bromide, m.p. 215° (*Ac* derivative, m.p. 157—158°; corresponding *perchlorate*, m.p. 153°), is most simply obtained by warming allyl bromide and $\text{C}_5\text{H}_5\text{N}$ in EtOH, cooling to 0° and adding PhCHO and 10*N*-NaOH. β -Hydroxy- β -*m*-hydroxyphenyl- α -vinylethylpyridinium bromide has m.p. (indef.) 195° (slight decomp.) or, after recrystallisation from 8*N*-HBr, m.p. 236° (decomp.); the *perchlorate* has m.p. 170°. Allylpyridinium bromide with the requisite aldehyde affords β -hydroxy- β -*o*-hydroxyphenyl-, m.p. 159—160° after softening, β -*m*-nitrophenyl-, m.p. 163—165°, β -*p*-nitrophenyl-, m.p. 203° (decomp.), and β -*m*-chlorophenyl-, m.p. 200—201°, α -vinylethylpyridinium bromide. β -Hydroxy- α - β -diphenylethylpyridinium bromide gives an acetate, m.p. 225° after softening, (also $+3\text{H}_2\text{O}$). The following *-ethylpyridinium bromides* are described: α -*m*-nitrophenyl- β -*o*-nitrophenyl-, m.p. 212°; β -hydroxy- α -phenyl- β -*o*-chlorophenyl-, m.p. 242°; β -hydroxy- β -*m*-nitrophenyl- α -methyl-, m.p. 212—214°; β -hydroxy- β -*p*-phenoxyphenyl-, m.p. 98—100°; β -hydroxy- β -*m*-bromophenyl-, m.p. 232—233° after softening. $\text{CH}_2\text{Ph}\cdot\text{CHO}$ and (I) give the known bromide (II) (*loc. cit.*), the mother-liquors of which give the *picrate*, m.p. 173.5°, of the diastereoisomeric form. The *picrate*, m.p. 108—113°, and the *perchlorate dihydrate*, m.p. 81—82°, corresponding with (II) have been prepared. $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ and boiling $\text{C}_5\text{H}_5\text{N}$ yield β -hydroxy- β -benzylethylpyridinium chloride, m.p. 142—143° (corresponding *picrate*, m.p. 161—162°). 3-Bromo-*N*-phenacylpyridinium bromide and the requisite aldehyde afford the following *-3-bromopyridinium bromides*: *N*- γ -trichloro- β -hydroxypropyl-, m.p. 215° (decomp.); β -hydroxy- β -*m*-nitrophenylethyl-, m.p. 261° (decomp.); β -hydroxy- β -phenylethyl-, m.p. 206—208°. *m*-Nitrophenacylphenyldimethylammonium enolbetaine and PhCHO in EtOH give α - β -oxido- β -*m*-nitrobenzoyl- α -phenylethane, m.p. 199°. α - β -Oxido- β -*m*-nitrobenzoyl- α -*m*-nitrophenylethane, m.p. 185°, and α - β -oxido- β -*p*-bromobenzoyl- α -*m*-nitrophenylethane, m.p. 131°, are described. The physiological action is discussed. H. W.

Reactivity of bromine atoms in brominated pyridines; formation of 6-bromo-1-methyl-2-pyridone from 2:6-dibromo-1-methylpyridinium salts. J. P. WIBAUT, B. W. SPEEKMAN, and H. M. VAN WAGTENDONK (Rec. trav. chim., 1939, 58, 1100—1104; cf. Decker *et al.*, A., 1911, i, 1023).—2:6-Dibromo-pyridine (I) and excess of Me_2SO_4 at 100° (bath) give the *-pyridinium methosulphate* [KI gives the iodide (II), m.p. 170° (decomp.), also obtained from (I) and MeI at 100°], converted by 10% aq. NaOH at room temp. into 6-bromo-1-methyl-2-pyridone (III), m.p. 105—105.5°. (II) similarly gives (III) and a substance, m.p. 177—178°. (III) and $\text{PBr}_3 + \text{PBr}_5$ at 190° give (I). The reaction mechanism is discussed. A. T. P.

Reactivity of bromine atoms in brominated pyridines. Formation of 4-bromo-2:6-diaminopyridine by action of ammonia on 2:4:6-tribromopyridine. J. P. WIBAUT, A. F. BICKEL, and L. BRANDON (Rec. trav. chim., 1939, 58, 1124—

1126).—2 : 4 : 6-Tribromopyridine with excess of aq. NH_3 (d 0.9) at 200° or with anhyd. liquid NH_3 (I) at $\sim 130^\circ$ (~ 90 atm.) gives 4-bromo-2 : 6-diaminopyridine (II), m.p. 126° ; with (I), a little dibromoaminopyridine, m.p. $155\text{--}158^\circ$, is also obtained. (II) is reduced ($\text{H}_2\text{--Ni}$; EtOH + a little aq. NaOH) to 2 : 6-diaminopyridine. A. T. P.

Synthesis of vitamin- B_6 . II. S. A. HARRIS and K. FOLKERS (J. Amer. Chem. Soc., 1939, 61, 3307—3310).—Variations and an improvement in the synthesis of vitamin- B_6 hydrochloride (I) (A., 1939, II, 340) are described. Hydrogenation (PtO_2) of the corresponding 5- NO_2 -compound in EtOH or AcOH gives 5-amino-3-cyano-6-methyl-4-ethoxymethyl-2-pyridone, m.p. $250\text{--}255^\circ$ (decomp.) [Ac, m.p. 260° (obtained best by effecting reduction in Ac_2O), and NN-Ac_2 derivative, m.p. 176° (obtained by an excess of boiling Ac_2O)], converted by $\text{PCl}_5\text{--POCl}_3$ at 30° into 6-chloro-3-amino-5-cyano-2-methyl-4-ethoxymethylpyridine (II) (16.5%) (Ac derivative, m.p. $134\text{--}136^\circ$). Hydrogenation (Pd-C-PtO_2) of the Ac_2 derivative, m.p. $90\text{--}92^\circ$, of (II) in $\text{AcOH}\text{--NaOAc}$ gives 3-diacyetyl-amino-2-methyl-5-aminomethyl-4-ethoxymethylpyridine [picrate, m.p. $190\text{--}191^\circ$ (36.4%)], hydrolysed by boiling 15% HCl to 3-amino-2-methyl-5-aminomethyl-4-ethoxymethylpyridine (III), $+\text{H}_2\text{O}$, m.p. $127\text{--}129^\circ$ (anhyd. dihydrochloride, m.p. $204\text{--}205^\circ$), which is best converted into (I) by hydrolysis by 2.5N- HCl at $175\text{--}180^\circ$ to 3-amino-2-methyl-5-aminomethyl-4-hydroxymethylpyridine dihydrochloride (IV), m.p. $235\text{--}237^\circ$, and a subsequent diazo-reaction. Alternatively, (III) is converted by boiling 48% HBr into 3-amino-2-methyl-4-bromomethyl-5-aminomethylpyridine dihydrobromide, m.p. $260\text{--}265^\circ$ (decomp.), and thence (hot H_2O ; AgCl) into (IV) and thence (I). 3-Hydroxy-2-methyl-5-hydroxymethyl-4-ethoxymethylpyridine hydrochloride (V), new m.p. $135\text{--}136^\circ$, with 2.5N- HCl at $155\text{--}160^\circ$ gives (I) (83%) or with conc. HCl at 132° gives 3-hydroxy-2-methyl-4 : 5-di(chloromethyl)pyridine hydrochloride, m.p. 206° , which with hot H_2O gives (I). The original prep. of (I) (*loc. cit.*) gives also a little 3-hydroxy-2-methyl-4 : 5-epoxydimethylpyridine hydrochloride, m.p. $239\text{--}240^\circ$, obtained also from (I) or (V) by 50% H_2SO_4 at 100° ; this is stable to 2.5N- HCl at 175° , but with boiling 48% HBr gives 3-hydroxy-2-methyl-4 : 5-di(bromomethyl)pyridine hydrobromide, new m.p. 228.5° . R. S. C.

Naphthyridine derivatives. III. Constitution of dihydroxyquinopyrin. Alcoholysis of quinolinimide. E. OCHIAI and I. IRAI (J. Pharm. Soc. Japan, 1939, 59, 152—155; cf. A., 1939, II, 452).—The ester, decomp. $219\text{--}220^\circ$ (acetate, m.p. 224°), of Fels (A., 1904, I, 617) is identical with Me 1 : 4-dihydroxy-2 : 5-naphthyridine-3-carboxylate of Ochiai *et al.* (*loc. cit.*). Quinolinimide, $\text{CH}_2\text{Br}\text{--CO}_2\text{Et}$, and KOH in boiling EtOH give 3-carbethoxypyridine-2-carboxylamide, m.p. 98° (also obtained as a by-product of the reaction of K quinolinimide and $\text{CH}_2\text{Br}\text{--CO}_2\text{Et}$), the structure of which is shown by conversion by NaOBr into 2-aminonicotinic acid, decomp. $295\text{--}296^\circ$. R. S. C.

Reduction of organic halogeno-compounds. XIV. Reduction of 2- $\gamma\gamma\gamma$ -trichloro- β -hydroxy-

propylpyridine. K. BRAND and K. REUTER (Ber., 1939, 72, [B], 1668—1678; cf. A., 1939, II, 307).—Reduction of 2- $\gamma\gamma\gamma$ -trichloro- β -hydroxypropylpyridine (I) with Zn and 10% H_2SO_4 and treatment of the product with 20% Na_2CO_3 gives 2- $\gamma\gamma$ -dichloro- β -hydroxypropylpyridine (II), m.p. 96° (hydrochloride, m.p. 107° ; aurichloride, m.p. $138\text{--}139^\circ$; platinichloride, m.p. 202° ; picrate, m.p. $102\text{--}103^\circ$). If the mixture is basified with 30% NaOH the product is indolizine (III), m.p. 75° , mixed with much resin. Electrolytic reduction of (I) at a Pb cathode with somewhat $>$ the calc. quantity of electricity and c.d. 2.3 amp. per sq. dm. gives (II) in $\sim 50\%$ yield; with more electricity the yield of (II) diminishes owing to the formation of a viscous oil whilst with a higher c.d. (III) is obtained in small amount. With Zn-Hg and the corresponding quantity of electricity the main product is (II); prolonged action followed by treatment of the cathode liquid with NaOAc affords compounds which give voluminous ppts. with picric and picronic acid but from which a homogeneous material could not be isolated. With Cu in presence of ZnCl_2 and c.d. 2.4 the main product is very pure (II), the same result being obtained at 100° and with a large excess of current. With c.d. 6 the production of (III) is not observed but the catholyte contains 2-propenylpyridine (IV) isolated as the picrate, m.p. $166\text{--}167^\circ$. (II) is also obtained in good yield by reduction of (I) at a Cu gauze cathode coated with Cd with c.d. 2.3; (III) and probably (IV) are also formed; similar results are obtained with c.d. 5.7 except that the yield of (II) is greatly diminished by the formation of resin. Electrochemical reduction of (I) is therefore similar to that of $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -diarylethanes, only 1 Cl being smoothly and readily removed. (I) is scarcely affected by Pb(OAc)_4 , Br-KOH , or fuming HNO_3 containing V_2O_5 at 100° . KMnO_4 oxidises (I) to CHCl_3 and pyridine-2-carboxylic acid possibly with intermediate production of 2- $\gamma\gamma\gamma$ -trichloro- β -ketopropylpyridine. 1-Methyl-2- $\gamma\gamma\gamma$ -trichloro- β -hydroxypropylpyridinium methosulphate, m.p. 146° (corresponding methiodide, m.p. $186\text{--}187^\circ$), is similarly oxidised by KMnO_4 . H. W.

Triboluminescence of substituted pyridines. K. KOKEGUTI (J. Pharm. Soc. Japan, 1939, 59, 134—135).—2 : 4-Distyrylpyridine (prep. from 2 : 4-dimethylpyridine, PhCHO , and a little ZnCl_2 at 240°), m.p. 174° (hydrochloride, m.p. $\sim 100^\circ$; picrate, m.p. 234° ; perchlorate, m.p. $229\text{--}230^\circ$), and 2 : 6-diphenylacetylenylpyridine show strong triboluminescence, though less than does 2 : 6-distyrylpyridine. 2-Styrylpyridine shows weak triboluminescence, 2-phenyl-4 : 6-distyryl- and 2 : 4 : 6-tristyryl-pyrimidine show none. R. S. C.

Exchange of hydrogen atoms between pyrrole [and] indole, and its methyl derivatives and water. VI, VII.—See A., 1940, I, 122.

Ethanolamines of the oxindole series. R. B. CRAWFORD and H. G. LINDWALL (J. Amer. Chem. Soc., 1940, 62, 171—173).—Condensation of the appropriate isatin derivative with MeNO_2 by a little NHET_2 in abs. EtOH at -15° gives 5-nitro-3-hydroxy-3-nitromethyloxindole, m.p. $145\text{--}147^\circ$, and its 1-Me,

m.p. 153°, and 1-*Et* derivative, m.p. 134—135°, and *Me* 3-hydroxy-3-nitromethyloxindole-7-carboxylate, m.p. 159—161.5°, and its 1-*Me*, m.p. 138—139°, and 1-*Et* derivative, m.p. 96—97.5°. Reduction by mossy Sn and HCl at <60° then gives 5-amino-3-hydroxy-3-aminomethyloxindole [dihydrochloride, m.p. >300°; picrate, m.p. 198° (decomp.); *Bz*₂, m.p. 249—251°; (*CO*₂*Et*)₂, m.p. 154°, and (*NH*₂·*CO*)₂ derivative, chars] and its 1-*Me* [dihydrochloride, m.p. 170—173°; picrate, m.p. 201—203° (decomp.); *Bz*₂, m.p. 249—251°; (*CO*₂*Et*)₂, m.p. 171—172°, and (*NH*₂·*CO*)₂ derivative, m.p. 213—214°] and 1-*Et* derivative [dihydrochloride, +2H₂O, m.p. 137—137.5°; picrate, m.p. 179—180°; *Bz*₂, m.p. 227—227.5°; (*CO*₂*Et*)₂, m.p. 183°, and (*NH*₂·*CO*)₂ derivative, m.p. 224—225°], and 3-hydroxy-3-aminomethyloxindole-7-carboxylic acid (hydrochloride, m.p. 187—188°; *Bz*, m.p. 240—241°, *CO*₂*Et*, m.p. 217—218°, and *NH*₂·*CO* derivative, m.p. 218—219°). R. S. C.

Compounds of sulphates of bivalent heavy metals with quinoline.—See A., 1940, I, 125.

Action of selenium on indoles, quinoline, and their hydrogenated derivatives. S. FUJISE and K. TIBA (Bull. Chem. Soc. Japan, 1939, 14, 478—482).—*trans*-6-Methyldecahydroquinoline with Se at 280—290° gives 6-methylquinoline (I) and its 5:6:7:8-H₂-derivative. Octahydro-2-methylindole hydrobromide and Se at 310—335° yield PhPr and 2-methylindole (II). Quinoline, (I), and (II) are unchanged when heated with Se at 310—320°, but indole yields H₂Se and a substance, m.p. 192—195°.

J. D. R.

Sulphides and sulphones of pyridine and quinoline. A. R. SURREY and H. G. LINDWALL (J. Amer. Chem. Soc., 1940, 62, 173—174).—2-Chloro-5-nitropyridine or 5-chloro-8- or 8-chloro-5-nitroquinoline and saturated, aq. Na₂S in boiling EtOH gives *di*-5-nitro-2-pyridyl sulphide (I), m.p. 136—137°, *di*-8-nitro-5-, m.p. 280—281°, and *di*-5-nitro-8-quinolyl sulphide (II), m.p. 288.5—290°, respectively. Oxidation of (I) by K₂Cr₂O₇ in aq. H₂SO₄ or of (II) by CrO₃ in AcOH gives *di*-5-nitro-2-pyridyl sulphone (III), m.p. 218.5—220.5°, and *di*-5-nitro-8-quinolyl sulphone, m.p. 260° (decomp. from 245°), respectively. With SnCl₂ (1 mol.) and HCl (I) and (III) give *di*-5-amino-2-pyridyl sulphide (IV), m.p. 130—131.5° (*Ac*₂ derivative, m.p. 265—266.5°), and sulphone, m.p. 238—239° (*Ac*₂ derivative, m.p. 276—278°), respectively, but with an excess of SnCl₂ (III) gives (IV). R. S. C.

Electron-sharing ability of organic radicals. X. α -Substituted tetrahydroquinolines. W. OLDHAM and I. B. JOHNS (J. Amer. Chem. Soc., 1939, 61, 3289—3291; cf. A., 1938, II, 300).—2-Ethylquinoline, prepared from quinoline by MgEtBr at 155°, and Na-EtOH give the 1:2:3:4-H₄-derivative, b.p. 110—113°/5 mm. (picrate, m.p. 119—120°). Quinaldine with NaNH₂, followed by PrⁿBr, gives 2-*n*-butylquinoline, b.p. 145—146°/11 mm. (picrate, m.p. 163—164°), reduced by Na-EtOH to the 1:2:3:4-H₄-derivative, b.p. 138°/6 mm. (*p*-C₆H₄Br·SO₂ derivative, m.p. 160—160.5°). LiAr and quinoline give the 2-aryldihydroquinolines, converted by distilling with Zn dust or heating with PhNO₂ into the 2-arylquinolines. 2-Phenyl-, m.p. 82.5° (picrate, m.p.

188.5—189°; *p*-C₆H₄Br·SO₂ derivative, m.p. 190—191°), 2-*p*-, m.p. 83° (picrate, m.p. 198.7°), and 2-*o*-tolyl-, m.p. 76—76.2°, b.p. 197°/4 mm. (picrate, m.p. 176°), and 2-mesityl-quinoline, m.p. 69—69.5°, b.p. 200°/4 mm. (picrate, m.p. 216.5°), with Na-EtOH give 2-phenyl-, b.p. 196°/8 mm. (picrate, m.p. 129°; *p*-C₆H₄Br·SO₂ derivative, m.p. 201—202°; also obtained by H₂-Pt-ZrO₂, whereas H₂-PtO₂ gives 2-cyclohexyldecahydroquinoline), 2-*p*-, b.p. 210°/14 mm. (picrate, m.p. 134—134.5°), and 2-*o*-tolyl-, m.p. 69.5°, b.p. 200—202°/6 mm., and 2-mesityl-1:2:3:4-tetrahydroquinoline, b.p. 218°/6 mm. Dissociation consts. of the above-mentioned tetrahydroquinolines, of the 2-*Me* and 2-*Et* analogues, and of 1:2:3:4-tetrahydroquinoline in MeOH are correlated with electron-sharing ability of the substituent as for the corresponding pyrrolidines (Goodhue *et al.*, A., 1934, 844; Kirchner, Diss., 1939). R. S. C.

Ammines containing 8-hydroxyquinoline and 5:7-dibromo-8-hydroxyquinoline.—See A., 1940, I, 129.

Spectrometry of complex salts of 8-hydroxyquinoline-5-sulphonic acid.—See A., 1940, I, 126.

Preparation of *py*-aminoquinolines and derivatives. R. R. RENSHAW and H. L. FRIEDMAN (J. Amer. Chem. Soc., 1939, 61, 3320—3322).—3-Aminoquinoline is obtained in 21% yield by condensing *o*-NH₂·C₆H₄·CHO and metazonic acid to 3-nitroquinoline and then reducing by SnCl₂-HCl, but is best prepared by treating quinoline with S and Br to give the 3-Br-derivative (50%), b.p. 158—162°/24 mm., which is then condensed (73% yield) with conc. aq. NH₃ and CuSO₄ at 160°. 3-Acetamidquinoline with HNO₃-AcOH gives the nitrate, m.p. 195.5° (decomp.), but with fuming HNO₃-H₂SO₄ gives (? 4-)nitro-3-acetamidquinoline, m.p. 205—206°, hydrolysed by KOH-EtOH to (? 4-)nitro-3-aminoquinoline, m.p. 189—189.5°, which could not be reduced and, when diazotised and then boiled in EtOH, gives (? 4-)nitro-3-ethoxyquinoline, m.p. 113—114°. Quinoline-2:4-dicarboxylic acid (*a*) in boiling PhNO₂ gives cinchonic acid (90%) and thence the 4-acid chloride hydrochloride, Me ester, b.p. 136—140°/4 mm., amide, m.p. 179—181°, and 4-amine, m.p. (+H₂O) 69° or (anhyd.) 154—156° (Ac derivative, m.p. 177—178°), and (*b*) affords the diacid chloride, Me₂, m.p. 131°, and Et₂ ester, m.p. 74—75.5°, di-anilide, m.p. 285—286°, and diamide, m.p. 277.5—279.5°, 2:4-diaminoquinoline, m.p. 197—198.5° (lit. 188—190°) [picrate, m.p. 283° (decomp.)], 4-carbethoxyquinoline-2-carboxylamide, m.p. 226—227.5°, and thence 2-aminocinchonic acid, m.p. 362° (decomp.), converted (diazo-reaction) into the 2-OH-acid or (soda-lime fusion) into 2-aminoquinoline. R. S. C.

Coupling reactions of aminoquinolines with benzenediazonium chloride. Orientation in the quinoline ring. R. R. RENSHAW, H. L. FRIEDMAN, and F. J. GAJEWSKI (J. Amer. Chem. Soc., 1939, 61, 3322—3326).—Coupling of aminoquinolines with diazo-compounds is almost always in accord with the static Erlenmeyer arrangement of ethylenic linkings, but its occurrence often depends on the conditions. In NaOAc-dil. AcOH or, less well, dil. HCl, the

appropriate aminoquinoline and PhN_2Cl give 6-amino-5-, m.p. 247—249° (hydrochloride, $+3\text{H}_2\text{O}$, m.p. 250—255°), 5-amino-8-, m.p. 191—194° (lit. 209—211°) (hydrochloride, m.p. 225—227°) (with, in HCl, some 6- PhN_2 -compound), 8-amino-5-, m.p. 133° (hydrochloride, m.p. 221—223°, hydrolysed in H_2O), and 7-amino-8-, m.p. 170—173° (hydrochloride, m.p. 210—211°), -benzeneazoquinoline. In aq. MeOH or abs. EtOH, 2-aminoquinoline gives 2-benzenediazo-aminoquinoline, m.p. 165—166.5°, but it does not react in aq. AcOH-NaOAc. In aq. AcOH-NaOAc or aq. MeOH, 3-aminoquinoline gives 3-benzenediazo-aminoquinoline, m.p. 156—157° (decomp.) or 177—178° (decomp.), in abs. EtOH gives 3-amino-4-benzene-azoquinoline, m.p. 198—201° (hydrochloride, m.p. 228—230°), but does not react in aq. HCl. 4-Aminoquinoline does not couple; with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ in abs. EtOH it gives a red compound, rapidly decomp. to yield PhNO_2 . 2:4-Diaminoquinoline does not couple in aq. HCl or abs. EtOH, and in aq. NaOAc-AcOH, aq. MeOH, or AcOH gives 4-amino-2-benzene-diazoaminoquinoline, m.p. 247.5—248.5°; 4-amino-2- p -nitrobenzenediazoaminoquinoline, m.p. 315.5—316.5° (hydrochloride, m.p. 323—325°), is similarly obtained in AcOH. The structure of the PhN_2 -compounds is proved by reduction (SnCl_2). The following are described, m.p. in brackets being those of the quinoxalines formed with phenanthraquinone: 5:6-, m.p. 135° (lit. 95°, 145°) [294—295° (lit. 287—288°)], 5:8-, m.p. 163°, 7:8-, m.p. 95—97° [314°], and 3:4-diaminoquinoline, m.p. 176—177° [280—281°] (Ac₂ derivative, m.p. 229—229.5°; obtained also from 3-bromo-4-aminoquinoline by 26% aq. NH_3 and CuSO_4 at 155—160°). R. S. C.

Sulphanilyl derivatives of pyridine and quinoline amines. R. WINTERBOTTOM (J. Amer. Chem. Soc., 1940, 62, 160—161).—2-, m.p. 190—191° [226—227°], and 3-sulphanilamidopyridine, m.p. 248—251° (decomp.) [272—275° (decomp.)], 2-amino-5-sulphanilamidopyridine, m.p. 210—211° [Ac₂ derivative, m.p. 288—291° (decomp.)], 3-, m.p. 185—186° (decomp.) [250—253° (decomp.)], 5-, m.p. 228—230° [256—258°], 6-, m.p. 202—204° [Ac derivative, m.p. 285—287° (hydrochloride, m.p. 238—240°)], and 8-sulphanilamidoquinoline, m.p. 194—195° [193—194°], are prepared. M.p. in brackets are those of the Ac derivatives. 7-Nitroquinoline, prepared (Skraup) from $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, but not by nitration with $\text{LiNO}_3\text{-Ac}_2\text{O}$ or $(\text{OH})_3\text{N}(\text{OAc})_2$, has m.p. 74—74.5°. Aminoquinolines are best prepared from the NO_2 -compounds by Raney Ni- H_2 . M.p. are corr. R. S. C.

Syntheses of heterocyclic derivatives of sulphanilamide. K. TSUDA, Z. ITIKAWA, and D. So (J. Pharm. Soc. Japan, 1939, 59, 155—158).—Condensation of $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ and the appropriate amine by NaHCO_3 in boiling COMe_2 and subsequent hydrolysis by 15% HCl (or HCl-MeOH) gives 2-sulphanilamido-pyridine, m.p. 189° (acetate, m.p. 227°), -quinoline, m.p. 195° (acetate, m.p. 241°), and -4-methylthiazole, m.p. 241°, 6-sulphanilamido-2-methyl-, m.p. 222°, and 2-amino-6-sulphanilamido-pyridine, m.p. 208° (acetate, m.p. 243°). R. S. C.

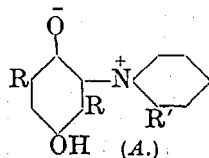
Synthesis of 4-aminohydrocarbostyryl and its derivatives. T. SASAKI and H. UEDA (Proc. Imp. G (A., II.)

Acad. Tokyo, 1939, 15, 315—320).— β -(o -Nitrophenyl)alanine (I) in NaOH with ClCO_2Me yields o -nitro- β -carbomethoxyaminohydrocinnamic acid, m.p. 165—166°, which is reduced (aq. $\text{NH}_3\text{-FeSO}_4$) to 4-carbomethoxyaminohydrocarbostyryl ($+0.5\text{H}_2\text{O}$), m.p. 127—129° (decomp.), converted by heating with aq. NaOH into carbostyryl (II). With $\text{Ac}_2\text{O-NaOH}$ (I) yields N -acetyl- β -(o -nitrophenyl)alanine, m.p. 177°, reduced (aq. $\text{NH}_3\text{-FeSO}_4$) to 4-acetamidohydrocarbostyryl, m.p. 233—234°. With $\text{CH}_2\text{Cl}\cdot\text{COCl}$ and NaOH, (I) yields N -chloroacetyl- β -(o -nitrophenyl)alanine, m.p. 178°, which with aq. NH_3 at 100° (sealed tube) yields N -glycyl- β -(o -nitrophenyl)alanine, ($+1.5\text{H}_2\text{O}$), m.p. 230° (decomp.) after sintering at 140—150°; this, when reduced ($\text{FeSO}_4\text{-aq. NH}_3$) yields, as sulphate (III), m.p. 220° (decomp.), 4-glycylaminohydrocarbostyryl, m.p. 147°. With BzCl and NaOH, (II) yields 4-hippurylaminohydrocarbostyryl, m.p. 227°. With BzCl-NaOH , (I) yields β -benzamido- o -nitrohydrocinnamic acid, m.p. 233°, which is reduced to 4-benzamidohydrocarbostyryl, m.p. 220—221°, hydrolysed by HCl into (II). (I) and $\text{ClCO}_2\text{CH}_2\text{Ph}$ in NaOH give o -nitro- β -carbobenzyloxyaminohydrocinnamic acid, m.p. 152°, reduced (Pd-H_2 in EtOH) to (II). J. D. R.

Polymerisation processes caused by pyridine.

III. Intermediates in the polymerisation of p -benzoquinone. O. DIELS and H. PREISS (Annalen, 1939, 543, 94—103; cf. A., 1937, II, 353).—A

solution of p -benzoquinone (I) in $\text{C}_5\text{H}_5\text{N}$ (prep. at 0°—room temp.) gradually deposits the betaine (II) (A, R = $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}^-$; R' = H), m.p. 217° (decomp.), which when heated in various solvents [e.g., $\text{C}_5\text{H}_5\text{N}$; $\text{HCO}_2\text{H-PhNO}_2$;



MeCN (repeated crystallisation necessary; one treatment only gives N-containing material)] affords trimeric (I), i.e., 2:5-di- p -hydroxyphenoxybenzoquinone (III) (compound, m.p. 250—255°, with $x\text{C}_5\text{H}_5\text{N}$). The diacetate of (III) is obtained from (II) and boiling $\text{Ac}_2\text{O-conc. H}_2\text{SO}_4$. 2-Methylpyridine (IV) and (I) similarly give a betaine [$+1$ mol. of (IV)] (A, R = $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}^-$; R' = Me), m.p. 187° (decomp.), which resembles (II); a 1:2 compound, decomp. 245° (blackens at 240°), of (III) and (IV) is described. The results with quinoline (V) and (I) are variable; a betaine could not be isolated but (III) and/or the compound, $p\text{-C}_6\text{H}_4(\text{OH})_2\cdot 2\text{C}_5\text{H}_7\text{N}$ (Baeyer *et al.*, A., 1902, i, 355) are formed. Prolonged interaction of thymoquinone and (I) affords a compound, $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}$, blackens at 205°. N -2':5'-Dihydroxyphenylquinolinium chloride, m.p. 274—275°, is obtained by concn. of a mixture of (I), (V), and $\text{CHCl}_3 + \text{conc. HCl}$. N -2':5'-Dihydroxyphenyl-2-methylpyridinium chloride and aq. Na_2CO_3 give the betaine ($+1.5\text{H}_2\text{O}$) (A, R = H, R' = Me), m.p. 217° (after loss of H_2O at 160—170°). H. B.

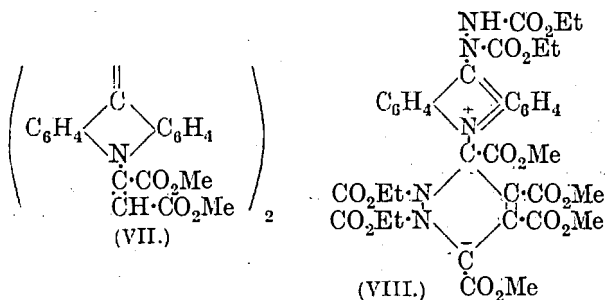
Heterocyclic compounds. X. Synthesis of substituted 1:2:3:4-tetrahydroacridones. W. BUKHSH and R. D. DESAI (Proc. Indian Acad. Sci., 1939, 10, A, 262—266).— $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ and Et cyclohexan-2-one-1-carboxylate in presence of a little conc. HCl at room temp. give Et 2- p -bromoanilino- Δ^1 -cyclohexene-1-carboxylate, m.p. 77—78°, which does

not give a colour with FeCl_3 and passes at 240—250° into 7-bromo-1:2:3:4-tetrahydroacridone, m.p. >350°. Similar transformations are *Et* 2-o-anisidino- Δ^1 -cyclohexene-1-carboxylate, m.p. 79—80°, into 5-methoxy-1:2:3:4-tetrahydroacridone, m.p. 277—279°, *Et* 2-p-anisidino- Δ^1 -cyclohexene-1-carboxylate, m.p. 71—72°, into 7-methoxy-1:2:3:4-tetrahydroacridone, m.p. 285—286°, *Et* 2-o-toluidino- Δ^1 -cyclohexene-1-carboxylate, m.p. 84—85°, into 5-methyl-1:2:3:4-tetrahydroacridone, m.p. 355—358°, and *Et* p-phenetidino- Δ^1 -cyclohexene-1-carboxylate, m.p. 88°, into 7-ethoxy-1:2:3:4-tetrahydroacridone, m.p. >350°. 2-Methylcyclohexanone and o- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ at 120° yield 1-o-carboxyanilino-6-methyl- Δ^1 -cyclohexene, m.p. 130°, which passes at 220° into 4-methyl-1:2:3:4-tetrahydroacridone, m.p. 345°. 1-o-Carboxyanilino-4-methyl- Δ^1 -cyclohexene, m.p. 143°, from 4-methylcyclohexanone, gives 3-methyl-1:2:3:4-tetrahydroacridone, m.p. >350°. *trans*-2-Ketodecahydronaphthalene yields 2-o-carboxyanilino- Δ^1 (or 2)-*trans*-octahydronaphthalene, m.p. 164—165° (also monohydrate, m.p. 82°), which gives Δ^1 (or 2)-octahydronaphthacridone, m.p. >350°. H. W.

Diene syntheses. XXXIII. Acridine and methyl acetylenedicarboxylate. O. DIELS and W. E. THIELE (Annalen, 1939, 543, 79—94).—Acridine (I) and $(\text{C}\cdot\text{CO}_2\text{Me})_2$ (II) in cold MeOH give a 1:1:1 adduct (*Me*₂ 5:10-dihydroacridine-5:10- $\alpha\beta$ -maleate methohydroxide) (III), red, m.p. 104° [converted by hot conc. HCl into 10-methylacridinium chloride (+3H₂O), m.p. 122° (decomp.)], together with a little of a yellow isomeric, m.p. 118°. In dioxan.

(I) and (II) afford the adduct (IV), red, m.p. 164—165°, and *Me*₂ 10-acridonylfumarate (V), yellow, m.p. 222—223° [hydrolysed (MeOH-KOH) to a dicarboxylic acid, $\text{C}_{17}\text{H}_{11}\text{O}_5\text{N}\cdot 1.5\text{H}_2\text{O}$, m.p. 225° (decomp.)]. Air slowly converts (III) (alone or in MeOH) into *Me*₂ 10-acridonylmaleate (VI), orange, m.p. 143° (rapid), 161° (slow heating) [hydrolysed to a dicarboxylic acid, $\text{C}_{17}\text{H}_{11}\text{O}_5\text{N}$, m.p. 255° (decomp.)], also obtained from (V) and hot $\text{C}_5\text{H}_5\text{N}$ or from (I), (II), and MeOH-H₂O₂. In Et₂O, (I) and (II) give (IV), (V), and (VI). Hydrolysis (aq. MeOH-KOH) of (III) affords a substance, $\text{C}_{16}\text{H}_{11}\text{O}_5\text{N}$, m.p. 241—242°. The 1:1:1 adduct, m.p. ~71°, from (I), (II), and EtOH when crystallised from MeOH yields (III); it is also converted [more rapidly than (III)] by air into (VI). Boiling MeOH-H₂O₂ transforms (III) into (VI) and a little of the diacridine (VII), m.p. 265—266°. Reduction (Zn dust, MeOH, conc. HCl) of (V) or (VI) gives a compound, $\text{C}_{38}\text{H}_{34}\text{O}_8\text{N}_2$, m.p. 260° (decomp.) [probably (VII) with $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot$ for $\text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Me})\cdot$]. Cold conc. H₂SO₄ rearranges (IV) by migration of the side-chain to C₁₁ and subsequent ring formation, to *Me*₄ 1':4'-dihydro-1:2-benzacridine 1':2':3':4'-tetracarboxylate, m.p. 189—190°. Hot HCO₂H converts (IV) into a *Me*₄ ester, $\text{C}_{17}\text{H}_9(\text{CO}_2\text{Me})_4$, m.p. 159—160°, probably a quinoline. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and (IV) in MeCN give a compound, $\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_9\cdot 1.5\text{H}_2\text{O}$; iso-

quinoline and *p*-O:C₆H₄:O (careful fusion) afford compounds, $\text{C}_{36}\text{H}_{31}\text{O}_8\text{N}_3$, m.p. 205°, and $\text{C}_{31}\text{H}_{25}\text{O}_{10}\text{N}$,



m.p. 232° (decomp.), respectively. $\text{C}_5\text{H}_5\text{N}$ and $(\text{CH}\cdot\text{CO})_2\text{O}$ (at 100—125° or in boiling PhMe) form 1:1 adducts, m.p. 123° and 259° (decomp.), respectively, with (IV) whilst $(\text{N}\cdot\text{CO}_2\text{Et})_2$ in boiling PhMe gives the compound (VIII), m.p. 203—204°. Structures are suggested for many of the above compounds.

H. B.

Anthraquinoneacridines.—See B., 1940, 119.

Benzanthrone-acridone.—See B., 1940, 120.

cycloTetramethylenepyrazolone. H. RUMKOPF (Ber., 1939, 72, [B], 1978—1982; cf. A., 1937, II, 307).—Treatment of *Et* cyclohexanecarboxylate (I) with the requisite substituted hydrazine in cold dioxan appears to give immediately 1-o-, m.p. 184°, 1-m-, m.p. 149.5°, and 1-p-tolyl-, m.p. 203°, 1-p-nitrophenyl-, m.p. 236°, and 1- β -naphthyl-, m.p. 180°, -3:4-cyclo-tetramethylenepyrazol-5-one. With $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NH}_2$ a comparatively stable hydrazone appears to result; it passes when recrystallised into 1- α -naphthyl-3:4-cyclo-tetramethylenepyrazol-5-one, m.p. 237°. 2:4-(NO₂)₂C₆H₃·NH·NH₂ yields exclusively *Et* cyclohexanecarboxylate-2:4-dinitrophenylhydrazone, m.p. 156°, which is unchanged at 160°. The action of halogens on derivatives of 3:4-cyclo-tetramethylenepyrazol-5-one gives unstable dihalides which readily give monosubstituted derivatives with loss of halogen acid in presence of H₂O. 4-Bromo-3:4-cyclo-tetramethylenepyrazol-5-one, m.p. 133°, 4-bromo-1-phenyl-, (II), m.p. 85°, -1-p-tolyl-, m.p. 94°, -3:4-cyclo-tetramethylenepyrazol-5-one, and 4-bromo-1-phenyl-2-methyl- Δ^6 -tetrahydro-[1':2'-benzo-3:4-pyrazol-5-one], m.p. 138°, are described. Chlorination in AcOH affords 4-chloro-3:4-cyclo-tetramethylenepyrazol-5-one, m.p. 112°. 4-Chloro-1-phenyl-, m.p. 70°, and 3:4-dichloro-1-phenyl-2-methyl-, m.p. 183° (decomp.), -3:4-cyclo-tetramethylenepyrazol-5-one have been obtained. (II) is converted by NH₃ or NHEt₂ in boiling MeOH into the compound, $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4$, m.p. 174° (decomp.), in 20—25% yield. This compound is also obtained when (I) is treated with Br and then distilled and the resulting *Et* cyclohexanecarboxylate is treated with NHPH·NH₂ in EtOH.

H. W.

ω -Amino-alcohols. I. 1-Phenyl-4- ω -hydroxyalkylpiperazines from ω -chlorohydrins. Derivatives of piperazine. XVII. G. W. ANDERSON and C. B. POLLARD (J. Amer. Chem. Soc., 1939, 61, 3439—3440; cf. A., 1939, II, 182).—1-Phenylpiperazine (2 mols.) and Cl-[CH₂]_n-OH (1 mol.) at 100° give 1-phenyl-4- δ -hydroxy-n-butyl-, m.p. 59—60° (91—92°),

- ϵ -hydroxy-*n*-amyl-, m.p. 74—75° (100—101.5°), - ζ -hydroxy-*n*-hexyl-, m.p. 65.5—67° (91.5—93°), - η -hydroxy-*n*-heptyl-, m.p. 75.5—76.5° (96.5—97°), - θ -hydroxy-*n*-octyl-, m.p. (anhyd.) 57—58.5° and (+H₂O) 80—82° (99.5—100.5°), - ι -hydroxy-*n*-nonyl-, m.p. 80—80.5° (94—95°), and - κ -hydroxy-*n*-decyl-piperazine, m.p. 67—68° (95—96°), m.p. in parentheses being those of the phenylurethanes. ζ -Chloro-*n*-hexyl-, m.p. 49—50°, and κ -chloro-*n*-decyl- α -naphthylurethane, m.p. 63—64°, and ι -chloro-*n*-nonylphenylurethane, new m.p. 70—70.5°, are reported. M.p. are corr.

R. S. C.

Pyrimidines. Synthesis from uracil of pyrimidines related structurally to thiamine. (Miss) D. RIEHL and T. B. JOHNSON (Rec. trav. chim., 1940, 59, 87—95).—Uracil and *N*-hydroxymethylbenzamide or -phthalimide with H₂SO₄ at room temp. give 5-benzamido-, m.p. 209—211° (decomp.), or -phthalimido-methyluracil (I), m.p. 254—255° (benzoyl- or phthaloyl-thymine), respectively, hydrolysed by boiling HCl to uracil. Neither is recommended as useful for synthesis of reduced pyrimidines related to thiamine. (I) and Br-H₂O give 5-bromo-4-hydroxy-5-phthalimidomethylhydrouacil, m.p. 278—282° (depends on rate of heating), also hydrolysed to uracil. (I) is decomposed by POCl₃, but a little reacts to give 2:6-dichloro-5-, readily decomposed to 2(? 6)-chloro-6(? 2)-hydroxy-5-phthalimidomethylpyrimidine, m.p. 150—155°; some ethoxymethylphthalimide is also obtained.

A. T. P.

Action of formamide on benzoin derivatives. Formation of diarylglyoxalines and tetra-arylpyrazines. A. NOVELLI (Anal. Asoc. Quim. Argentina, 1939, 27, 161—168).—Anisoin with HCO₂H and (NH₄)₂CO₃ yields 4:5-di-(*p*-methoxyphenyl)glyoxaline, m.p. 183—184°, and 2:3:5:6-tetra-(*p*-methoxyphenyl)pyrazine, m.p. 282—283°. Similarly benzoin gives 4(or 5)-phenyl-5(or 4)-(*p*-methoxyphenyl)glyoxaline, m.p. 214—215°, and 2:5-tetra-(*p*-methoxyphenyl)pyrazine, m.p. 183—184°, whilst *p*-toluoin yields 4:5-di-(*p*-tolyl)glyoxaline, m.p. 275—276°, and 2:3:5:6-tetra-(*p*-tolyl)pyrazine, m.p. 295—296°. Furoin gives only decomp. products. The mechanism of the reaction is discussed.

F. R. G.

Laboratory experiments in organic chemistry. II—IV. Preparation of lysidine, 2:3-dihydro-5:6-diphenylpyrazine, and 2:3-diphenylpyrazine. L. H. AMUNDSEN (J. Chem. Educ., 1939, 16, 566—567; cf. A., 1937, II, 232).

L. S. T.

Seven-membered heterocyclic ring compounds from *o*-phenylenediamine and acetylacetone derivatives. S. B. VAISMAN (Trans. Inst. Chem. Charkov Univ., 1938, 4, No. 13, 157—174).—*o*-C₆H₄(NH₂)₂ and CHMeAc₂ in AcOH-EtOH yield a colourless base, m.p. 86°, giving a red hydrochloride: *o*-C₆H₄ $\left\langle \begin{smallmatrix} \text{N:CMe} \\ \text{N:CMe} \end{smallmatrix} \right\rangle$ CHMe (+ HCl) \rightarrow [*o*-C₆H₄ $\left\langle \begin{smallmatrix} \text{NH:CMe} \\ \text{NH:CMe} \end{smallmatrix} \right\rangle$ CMe]⁺Cl⁻. With CMe₂Ac₂ the product is the coloured base, *o*-C₆H₄ $\left\langle \begin{smallmatrix} \text{N:CMe} \\ \text{N:CMe} \end{smallmatrix} \right\rangle$ CMe₂ (acetate, m.p. 220°).

R. T.

G* (A., II.)

cis-Indigotin. II. G. HELLER (Ber., 1939, 72, [B], 1858—1860; cf. A., 1936, 615).—*cis*-Indigotin (I) is obtained by dissolving indigo powder (II) in NaOH-Na₂S₂O₄ at room temp., filtering the diluted solution, and shaking the cold filtrate with air; the product is collected, washed, and dried in a vac. over H₂SO₄. *trans*-Indigotin (III) is obtained from the above solution and air at 100°. Dioxan is scarcely coloured by (III) whereas (I) gives a distinct blue solution; the colour begins to fade after ~2 min. A similar but less pronounced behaviour is observed in CCl₃CO₂H or AcOH-conc. H₂SO₄ (87.5:12.5). Solid (I) appears to pass into (III) within 24 hr. The prep. of indigo-oxime from (II) is described. H. W.

Colour of 4-hydroxy-2-thio-3-aryl-1:2:3:4-tetrahydroquinazoline. L. MANOLESCU-PAVLESCU (Bull. Acad. Sci. Roumaine, 1938, 20, 28—29).—Derivatives of 2-thio-3-aryl-1:2:3:4-tetrahydroquinazoline (I) or their Hg halide salts (II) give coloured derivatives similar to the 2-keto-analogues, which indicates that the bathochromic effects of CO and S·HgX are similar. When (II) are heated in solution quinones result. Derivatives of 4-hydroxy-2-thio-3-aryl-1:2:3:4-tetrahydroquinazoline and the corresponding 2-keto-compounds give red and yellow Hg halide salts, respectively. The bathochromic effect of S is > that of O and in either series the effect of I > Br > Cl. 4-Ethoxy-2-thio-3-phenyl-1:2:3:4-tetrahydroquinazoline with AgNO₃ gives a colourless complex salt which with H halides forms a colourless and a coloured salt. The 3-*o*- and -*p*-tolyl analogues of (I) and AgNO₃ give yellow compounds. ·S and ·SH have positive auxochromic effects.

J. L. D.

Conversion of chlorophyll into phaeophytin. G. MACKINNEY and M. A. JOSLYN (J. Amer. Chem. Soc., 1940, 62, 231—232).—Removal of Mg from chlorophyll-*a* by acid is 7—9 times as fast as from -*b* (cf. A., 1938, II, 296) and is a first-order reaction with respect to acid and (probably) chlorophyll.

R. S. C.

Chlorophyll. XCIII. γ -Formylpyrroporphyrin. H. FISCHER and E. STIER (Annalen, 1939, 542, 224—240).—It has not been possible to convert the γ -Me of phylloporphyrin into CH₂·CO₂H. Phylloporphyrin Me ester (I) is oxidised [I in AcOH-NaOAc at 100° (bath); product treated with Et₂O-CH₂N₂] to γ -formylpyrroporphyrin Me ester (II), m.p. 244° (Cu salt, m.p. 203°), also obtained (no details) from γ -formylpyrrochlorin Me ester (A., 1937, II, 470). The oxime, m.p. 277°, of (II) with boiling Ac₂O + NaOAc gives γ -cyanopyrroporphyrin Me ester, m.p. 261°, whilst (II) and boiling 30% MeOH-KOH afford pyrroporphyrin (III). Reduction (H₂-PtO₂ in dioxan for 4 days) of (II) (as Zn salt) gives, after removal of Zn with 18% HCl, γ -hydroxymethylpyrroporphyrin Me ester, m.p. 236°. The unstable cyanohydrin from (II) and anhyd. HCN in C₅H₅N + anhyd. Na₂CO₃ is converted by MeOH-HCl into a complex mixture of porphyrins. Me₂ pyrroporphyrin- γ -glyoxylate (IV), m.p. 248°, obtained by oxidation (I-AcOH-NaOAc) of isochlorophyrin-*e*, Me₂ ester [= γ -carbomethoxymethylpyrroporphyrin] (V), is reduced [as for (II) or by H₂-Pd-BaSO₄ in HCO₂H at 65°] to Me₂ pyrro-

porphyrin-γ-glycollate, m.p. 278°. Boiling 30% MeOH-KOH in N₂ converts (IV), but not (V), into (III). Reduction (H₂, Pd, HCO₂H, 65°) of (II) gives (I); phæoporphyrin-*a*₅ Me₂ ester and its 10-OAc-derivative (VI) similarly (at 55–60°) afford some *deoxophæoporphyrin-a*₅ Me₂ ester, m.p. 289°, and its 10-OAc-derivative, respectively, but in cold HCO₂H (VI) appears to give 9-hydroxydeoxo-10-acetoxyp hæoporphyrin-*a*₅ (VII) (cf. A., 1935, 362). The Fe complex salt of pyrroporphyrin-*γ*-glycollic acid and SnBr₄ in CHCl₃·OEt give a small amount of a porphyrin nearly identical with (VII). H. B.

Magnetic properties of ethylcarbimideferro-hæmoglobin and iminazole-ferrihæmoglobin.—See A., 1940, 1, 15.

Constitution of the prosthetic group of cytochrome-c. K. ZEILE and H. MEYER (Naturwiss., 1939, 27, 596–597).—The compound of HBr with protoporphyrin (I) fused with *l*-cysteine Me₃ ester hydrochloride yields the compound, C₄₄H₅₆O₈N₆S₂, [α]_D²⁰ +27° in 0.1% HCl, also obtained (+1H₂O), [α]_D²⁰ –172° in 0.1% HCl, by hydrolysing cytochrome-c in 2 × 10⁻⁵M. solution, methylating, and fractionating; the absorption spectra are identical. Hence the prosthetic group of cytochrome-c is a compound of (I) with 2 mols. of cysteine. The complex Fe salt of the compound yields, on reduction (neutral) without addition of N base, a hæmochromogen having chief absorption bands in the same positions as those of cytochrome-c. In the hæmochromogen the 6 co-ordinate linkings of the Fe are united to the N of the hæm mol. and to those of the cysteine-NH₂ in the side-chains. The N of the cysteine-NH₂ takes part thus in hæmochromogen production only with hæm present in the same mol. W. McC.

Phthalocyaninesulphonyl chlorides.—See B., 1940, 122.

Ionisation constants and hydrolytic degradations of cyameluric and hydromelonic acids. C. R. REDEMANN and H. J. LUCAS (J. Amer. Chem. Soc., 1939, 61, 3420–4325).—The formulæ of Pauling *et al.* (A., 1938, I, 122) for hydromelonic (I) and cyameluric acid (II) are supported. Electrometric titration (glass electrode) of the K salt by HCl shows (I) to be a much stronger acid than (II). K melonate and boiling 6N-HNO₃ give 72.5% of cyanuric acid (III), some further hydrolysis also occurring; alkaline hydrolysis gives 2.24 NH₃ for each CO₂ liberated, the reaction thus being K₃C₆N₁₃ + 6KOH + 6H₂O → K₃C₆H₃N₇ + 6NH₃ + 3K₂CO₃. Conc. HNO₃ hydrolyses (II) to (III) in 93.5% yield. Prep. of the substances named and of melon and Na cyamelurate, +5.5H₂O, is described. R. S. C.

Reaction between hydrogen selenide, formaldehyde, and sec. amines. A. H. BRNZ, F. E. REINHART, and H. C. WINTER (J. Amer. Chem. Soc., 1940, 62, 7–8).—1-Hydroxymethylpiperidine (prep. described) or 4-hydroxymethylmorpholine and H₂Se in dry Et₂O-N₂ give *di*-1-piperidino-, m.p. 67°, and *di*-4-morpholino-methyl selenide (I), m.p. 136–138°, respectively, both stable in air when solid and in EtOH or C₆H₆ in absence of air, but unstable in H₂O, and toxic to rats. (I) is best prepared by saturating

aq. morpholine with H₂Se and pouring the solution into aq. CH₂O. 98.1% of the Se is pptd. when (I) is aerated in 80% EtOH at 40°. Aq. H₂O₂ gives a stable, colloidal solution of Se. R. S. C.

αω-Amino-alcohols. II. Morpholino-alcohols. Derivatives of morpholine. II. G. W. ANDERSON and C. B. POLLARD (J. Amer. Chem. Soc., 1939, 61, 3440–3441; cf. A., 1938, II, 71).—Morpholine, Cl·[CH₂]_n·OH, and Cu chromite in dioxan at 235–270°/100 atm. give 4-8-hydroxy-*n*-butyl-, b.p. 116.5–117°/5 mm. (*phenylurethane*, m.p. 86–87°), 4-ε-hydroxy-*n*-amyl-, b.p. 133–133.5°/5 mm. (*phenylurethane*, m.p. 55.5–57°), 4-ζ-hydroxy-*n*-hexyl-, b.p. 146–147°/5 mm. (*α-naphthylurethane*, m.p. 71–72°), 4-η-hydroxy-*n*-heptyl-, b.p. 155.5–158°/5 mm. (*phenylurethane*, m.p. 71–72°), 4-θ-hydroxy-*n*-octyl-, b.p. 164–164.2°/5 mm. (*α-naphthylurethane*, m.p. 73–74°), 4-ι-hydroxy-*n*-nonyl-, b.p. 173–173.5°/5 mm. (*α-naphthylurethane*, m.p. 54–56°), and 4-κ-hydroxy-*n*-decyl-, b.p. 164–165°/2 mm. (*α-naphthylurethane*, m.p. 66.5–67.5°), -morpholine with αδ-*n*-butylene-, m.p. 51.5–52.5°, b.p. 147.5–148.5°/5 mm., αε-*n*-amylene-, b.p. 161–162°/5 mm., αζ-*n*-hexylene-, m.p. 35.5–38.5°, b.p. 169.5–171°/5 mm., αη-*n*-heptylene-, b.p. 183–184°/5 mm., αθ-*n*-octylene-, double m.p. 46.5–47.5° and 48°, b.p. 191.5–193.5°/5 mm., αι-*n*-nonylene-, b.p. 203.5–204°/5 mm., and ακ-*n*-decylene-, double m.p. 48–49° and 50.5–51.5°, b.p. 187–189°/2 mm., -4:4'-dimorpholine, respectively. M.p. of the urethanes are corr. R. S. C.

[Substitution of thiazole.] J. P. WIBAUT (Ber., 1939, 72, [B], 1708; cf. Ochiai and Nagasawa, A., 1939, II, 455).—The resemblance between thiazole and C₅H₅N has been noted previously by Wibaut *et al.* (A., 1932, 522, 1260; 1934, 309; 1937, II, 350). Ochiai's statement that thiazole derivatives cannot be halogenated if the C₂ position is unoccupied is not valid. Bromination occurs at C₂ but a high temp. is necessary. At lower temp. additive products resembling perbromides result. This is also the case with C₅H₅N. H. W.

2-Sulphanilamidothiazole: a new chemotherapeutic agent. W. A. LOTT and F. H. BERGHEIM (J. Amer. Chem. Soc., 1939, 61, 3593–3594).—2-Sulphanilamidothiazole ["sulphathiazole"], m.p. 197–197.5° (uncorr.), 202–202.5° (corr.) [Na salt, m.p. 256–256.5° (uncorr.), 264.5–265° (corr.)]; hydrochloride, m.p. 193–197° (uncorr.)] (cf. Fosbinder *et al.*, A., 1939, II, 525), is less acidic than is "sulphapyridine." Both compounds can be determined by Marshall's method (A., 1938, III, 972). They can be distinguished by formation of purple and brown Cu salts, respectively. R. S. C.

Benzthiazyl alkyl sulphides.—See B., 1940, 119.

Semiquinone radicals of the thiazines. L. MICHAELIS, M. P. SCHUBERT, and S. GRANICK (J. Amer. Chem. Soc., 1940, 62, 204–211).—Thionine gives a semiquinone radical as intermediate between the dye and the leuco-compound. Only a few % of this exists in the *p*_H range of normal buffers, but in conc. acid (10–26N-H₂SO₄) it is identified by the reductive titration curve, its yellow colour, and characteristic absorption (strong bands at 440 and

496, weaker bands at 476, 460, and 510 m μ .). Methylene-blue forms a similar radical, which, however, requires even more conc. acid for stability. The radical owes its stability to equiv. resonance (of the same type as is shown by Wurster radicals), which can develop only after addition of two protons. The radical, as an intermediate stage in the reduction of the dye, accounts for the reversibility of the reduction and the catalytic effect of the dyes in biological reactions.

R. S. C.

Cyanine types.—See B., 1940, 121.

Tobacco alkaloids. XVI. 1-Methylpyrrolidine, a new tobacco alkaloid. Constitution of isonicotine. E. SPÄTH and S. BINIECKI (Ber., 1939, 72, [B], 1809—1815).—The readily volatile tobacco bases are treated with p -C₆H₄Me·SO₂Cl for the removal of primary and sec. bases; the residual *tert.* bases are liquefied by strong cooling and then warmed to room temp., whereby NMe₃ is mainly evolved. In the residual bases the presence of 1-methylpyrrolidine is established by the isolation of its hydrochloride, trinitro-*m*-tolylxide, picrate, and aurichloride. The isonicotine of Noga (A., 1915, i, 711) is identified as 2:3'-dipyridyl, which is very hygroscopic. A mixture of *l*-anabasine (I) and lupinine (II) can be isolated by distillation from the alkaloid mixture from *Anabasis aphylla*, L.; from it (I) can be isolated as the picrate which is relatively sparingly sol. in H₂O, in which the picrate of (II) is sol.

H. W.

Alkaloids of the fruit of *Orixa japonica*, Thunb. T. OBATA (J. Pharm. Soc. Japan, 1939, 59, 136—138).—Extraction of this fruit with MeOH yields kokusagin, m.p. 192—193° (picrate, m.p. 157°), and skimmiamine, m.p. 177° (picrate, decomp. 189—190°) (cf. Asahina *et al.*, A., 1930, 1454). Mel at 100° converts the latter alkaloid into a product, C₁₂H₇O₂N(OMe)₂, m.p. 187°, converted by HI-Ac₂O into a substance, m.p. >315°, or by KMnO₄ in warm COMe₂ into an aldehyde, C₁₀H₄O₂N(OMe)₃, decomp. 241° (phenylhydrazine, decomp. 195°), and an acid, C₁₀H₄O₃N(OMe)₃, decomp. 250° (obtained also by further oxidation of the aldehyde). Boiling, conc. HCl converts the acid into CO₂ and a substance, C₉H₅O₂N(OMe)₂, m.p. 248°.

R. S. C.

Lupine. XIV. Isolation of anagryne from *Lupinus laxiflorus*, var. *silvicola*, C. P. Smith. J. F. COUCH (J. Amer. Chem. Soc., 1939, 61, 3327—3328; cf. A., 1939, II, 456).—This plant contains 0.7—1.0% of alkaloids, mainly anagryne, $[\alpha]_D^{25}$ -168° in EtOH [hydrochloride, m.p. (+3H₂O) 235—236°, (+0.5H₂O) 284.5—285.5° (corr.), (anhyd.) 295—297°, $[\alpha]_D^{25}$ (+0.5H₂O) -124.2° in H₂O; perchlorate; aurichloride, m.p. 167—168°; picrate, m.p. 169.5°; methiodide, m.p. 262—263° (corr.)], but no cytisine, methyleytisine, or sparteine.

R. S. C.

Complete conversion of *l*-ecgonine methyl ester into *l*-cocaine. A. W. K. DE JONG (Rec. trav. chim., 1940, 59, 27—30).—*l*-Ecgonine Me ester, BzCl, and dry Na₂CO₃ or CaO or CaO + Ca(OH)₂ in Et₂O, CHCl₃, or best in anhyd. C₆H₆ (10 hr.) give complete conversion into *l*-cocaine.

A. T. P.

Alkaloids of *Roemeria refracta*, D.C. Constitution of roemerine and synthesis of 2:3-methylenedioxyphenanthrene. IV. Alkaloids of Papaveraceæ family. R. KONOVALOVA, S. JUNUSSOV, and A. P. OREKHOV (Bull. Soc. chim., 1939, [v], 6, 1479—1485; cf. A., 1939, II, 565).—6-Nitropiperonal and CH₃Ph·CO₂H-Ac₂O at 100° (bath) give 6-nitro-3:4-methylenedioxy- α -phenylcinnamic acid, m.p. 199—200°, reduced by FeSO₄-aq. NH₃ at 80°, then 100°, to the 6-NH₂-derivative, m.p. 207—208°, which is converted by diazotisation, followed by Cu, into 2:3-methylenedioxyphenanthrene-9-carboxylic acid, m.p. 255—256°, decarboxylated (Cu chromite-quinoline) to 2:3-methylenedioxyphenanthrene (I), m.p. 99—100° (picrate, m.p. 149—150°; dibromide, m.p. 228—229°), not identical with the isomeride from roemerine (*loc. cit.*). (I) is hydrolysed by HCl (d 1.18) at 140—150° to the 2:3-(OH)₂-derivative, methylated (CH₃N₂) to 2:3-dimethoxyphenanthrene, m.p. 131—132° (dibromide, m.p. 159—160°). The isolation of *l*-ephedrine and *l*- ψ -ephedrine from the plant is confirmed (*loc. cit.*).

A. T. P.

Alkaloids of the morphine group. I. Synthesis of aminocodide. E. OCHIAI and S. YOSHIDA (J. Pharm. Soc. Japan, 1939, 59, 127—128).—Bromocodide is converted by NH₃-EtOH at 100° into the non-cryst. aminocodide (Ac derivative, decomp. 117°; carbamido-compound, m.p. 238—240°).

H. W.

Dissociation constants and titration exponents of less common alkaloids.—See A., 1940, I, 73.

Modified Bart reaction. G. O. DOAK (J. Amer. Chem. Soc., 1940, 62, 167—168).—Addition of saturated aq. NaNO₂ (1 mol.; starch-KI) and then CuBr to the amine, H₂SO₄, and AsCl₃ in abs. EtOH gives the following yields of C₆H₄R·AsO₃H₂: R = *p*-57 and *m*-SO₂·NH₂ [melts at 218—219° (slow heating from 215°), resolidifies forming an anhydride of indefinite m.p.] 58, *m*-NO₂ 54, and *m*-CO₂H 76, and 2:1:4-NO₂·C₆H₃Me·AsO₃H₂ 76%, the respective yields by the ordinary Bart procedure being 25, 0, 28, 36.6, and 15.5%.

R. S. C.

Preparation of phenylarsinoxides. I. Mono-substituted derivatives. G. O. DOAK, H. EAGLE, and H. G. STEINMAN (J. Amer. Chem. Soc., 1940, 62, 168—170).—*p*- and *o*-NO₂·C₆H₄·AsO₃H₂ with SO₂-KI give *p*- and *o*-nitrophenylarsinoxide (Na₂ salt, +2H₂O), respectively, but the *m*-acid gives *m*-nitrophenylarsinoxide hydrate (not readily dehydrated). Reduction of *m*-NH₂·C₆H₄·AsO₃H₂ in conc. HCl gives the dichloroarsine, converted by NH₃ into *m*-aminophenylarsinoxide, softens at 62° (corr.). *m*-, +2H₂O, and *o*-hydroxy-, *m*- and *o*-chloro-, softens at 208° (corr.), *o*-sulpho- (Na salt), and *o*-iodo-phenylarsinoxide, softens at 263°, m.p. 267°, and *o*-sulphophenylarsinic acid (Na₂ salt, +H₂O) are also described.

R. S. C.

Condensation of arsenic chloride with dialkyl aromatic amines. P. S. VARMA, K. S. V. RAMAN, and (Miss) K. M. YASHODA (J. Indian Chem. Soc., 1939, 16, 515—518).—NPhMeEt and AsCl₃ give *p*-methylethylaminophenylarsinoxide, m.p. 74—75° (sulphide, m.p. 157°; chloride hydrochloride, m.p. 99°; bromide hydrochloride, m.p. 143°; iodide hydrochloride,

decomp. readily; *arsinic acid*, m.p. $>250^\circ$, and *tri- p -methylethylaminophenylarsine*, m.p. 206° . Similarly α -C₁₀H₇NMe₂ yields 1-dimethylaminonaphthyl-4-*arsin-oxide*, m.p. 98—100° (sulphide, m.p. 144° ; *chloride hydrochloride*, m.p. 110—112°; *bromide hydrochloride*; *iodide hydrochloride*, m.p. 119—120°), and *tri*-(1-dimethylaminonaphthyl)-4-*arsine*, m.p. 148° ; *m*-C₆H₄MeNMe₂ yields 4-dimethylamino-2-methylphenyl-*arsin-oxide*, m.p. 108° (sulphide, m.p. 137° ; *arsinic acid*, m.p. $>250^\circ$), and *tri*-4-dimethylamino-2-methylphenyl-*arsine*, m.p. 98° ; *p*-C₆H₄MeNMe₂ yields 2-dimethylamino-5-methylphenyl-*arsin-oxide*, m.p. 63—65° (sulphide, m.p. 68° ; *arsinic acid*, m.p. $>250^\circ$).

F. R. G.

Synthesis of organobismuth compounds. H. GILMAN and A. C. SVIGON (J. Amer. Chem. Soc., 1939, 61, 3586).—(ArN₂Cl)₃.BiCl₃ complexes (e.g., Ar = *p*-C₆H₄Me) and Cu powder in cold COMe₂ give BiAr₃.

R. S. C.

Hydrolysis of gelatin by enzymes and by heating under pressure.—See A., 1940, III, 163.

Proteins in liquid ammonia. V. Reaction of sodium in liquid ammonia with peptones and related substances. C. O. MILLER and R. G. ROBERTS (J. Amer. Chem. Soc., 1939, 61, 3554—3556; cf. A., 1936, 492).—When Na is added to peptones (I) in liquid NH₃, evolution of H₂ becomes rapid only after a definite amount of Na has been added and reaches a max., not altered by addition of further Na. (I) thus differ from proteins (II) or NH₂-acids (III). Diketopiperazines (IV) liberate no H₂ and greatly decrease the amount liberated from (II), possibly by complex-formation. (I) are more acidic (to Na) than are (II) or (III). Silk-(I), when digested with H₂SO₄, have min. acidity after 2—3 days; after 10 days they behave as (III); (IV) may be present in quantity on the second and third days. (I) in liquid NH₃ probably contain more (IV) than do (II). (II) probably owe their acidity to juxtaposition of NH and aryl by ring-crumpling.

R. S. C.

Quantitative absorption spectrophotometry.—See A., 1940, I, 133.

Stability of colour produced by Nessler's reagent.—See A., 1940, III, 176.

Modified Beilstein test for halogens in organic compounds. D. F. HAYMAN (Ind. Eng. Chem. [Anal.], 1939, 11, 470).—The compound is burned under a red-hot monel metal tube; halogen is indicated by a green-blue flare as the decomp. products touch the tube. The test is negative with certain types of pyrimidines, pyridines, and hydroxyquinolines which give a strongly positive Beilstein test.

J. D. R.

Behaviour of the SMe group during the methoxyl determination. F. ARNDT, L. LOEWE, and M. OZANSOY (Ber., 1939, 72, [B], 1860—1863).—SMe of methionine is somewhat more slowly hydrolysed than OMe with HI. *p*-C₆H₄Me-SMe is only very slowly attacked and *p*-C₆H₄Me-SH, if formed, undergoes extensive decomp. Still greater difficulty is experienced with AcSMe and *S*-methylisothiocarbamide sulphate. Complete similarity to OMe is shown by SMe in thiourazole Me ether and its

4-Ph derivative. Dithiourazole Me₂ ether slowly suffers complete hydrolysis but this is not the case with iminothiotriazolethiol Me ether.

H. W.

Determination of organic peroxides. H. A. LIEBHAFSKY and W. H. SHARKEY (J. Amer. Chem. Soc., 1940, 62, 190—192).—The sample is added to a mixture of glacial AcOH, NaHCO₃, KI, and Na₂S₂O₃, kept in the dark for 5 min., and the I then titrated. When KI₃ solution is added to excess of Na₂S₂O₃ in glacial AcOH, the colour fades at a measurable rate. Bz peroxides and the peroxides in Bu₂O are equally reactive towards iodide in AcOH, and slightly less reactive than H₂O₂ in AcOH. H₂O retards all three reactions.

W. R. A.

Determination of furfuraldehyde in furfuraldehyde-furfuryl alcohol solution. A. P. DUNLOP and F. TRIMBLE (Ind. Eng. Chem. [Anal.], 1939, 11, 602—603).—A modification of the NaHSO₃-I method is described.

S. M.

Electrometric determination of thiolbenzthiazole. P. G. SPACU (Bull. Acad. Sci. Roumaine, 1939, 22, 142—145).—The sample in 76—80% aq. COMe₂ is titrated potentiometrically with 0.1N-AgNO₃. A considerable rise in potential occurs at the equivalence point. It is advisable to keep the solution for 2—5 min. when near the end-point before reading the potential.

J. W. S.

Precipitation of alkaloids by cuprous chloride. J. J. L. ZWIKKER and A. KRUYSE (Pharm. Weekblad, 1940, 77, 18—22).—Aconitine, apomorphine, berberine, brucine, cevadine, cinchonidine, cinchonine, cocaine, codeine, caffeine, cotarnine, dionine, emetine, heroine, hydrastine, quinidine, quinine, narceine, narcotine, papaverine, strychnine, thebaine, theophylline, veratrine, yohimbine, and CH₂Cl₂N₄ (1:50,000) give cryst. ppts. (1:1000) when treated with 0.25 vol. (4 vols. for cinchona alkaloids) of a reagent consisting of cryst. CuCl₂ (200), Na₂SO₃.7H₂O (250 mg.), and 2N-HCl (2 c.c.) in H₂O (10 c.c.). No ppt. is formed with adrenaline, atropine, colchicine, coniine, cytisine, ephedrine, homatropine, morphine, nicotine, novocaine, eserine, pilocarpine, piperine, scopolamine, solanine, sparteine, tropine, NHPhAc, antipyrine, pyramidone, tyrosine, CO(NH₂)₂, or urethane. The ppts. disappear when the mixtures are exposed to air.

S. C.

Two precipitation reactions of organic arsenic compounds. M. PÉRONNET and R. H. RÉMY (J. Pharm. Chim., 1939, [viii], 30, 353—364).—10% EtOH and 10% aq. EtOH solutions of many org. As^{III} and As^V compounds (or saturated solutions of the less sol. compounds) are treated with 1 drop of a saturated COMe₂ or aq. solution of H₂S, or with a Hg(NO₃)₂ reagent, and the ppts. observed. In EtOH, only *p*-NO₂-C₆H₄-AsCl₂ and *p*-C₆H₄(AsO)₂ yield ppts. with the H₂S reagent, whereas in aq. EtOH all the chloroarsines and arsine oxides gave ppts.; *p*-nitrophenarsazine chloride, AsPh₂O-OH, and ArAsO₃H₂ do not react. The Hg(NO₃)₂ reagent reacts better with EtOH solutions; the configurations As(Alk)₂ and As(Alk)₃ are not pptd. The reactions with various As compounds are tabulated and their sensitivity is discussed.

J. L. D.

A., II.—Organic Chemistry

APRIL, 1940.

Applications of selenium dioxide to the oxidation of organic compounds. Y. MAYOR (Chim. et Ind., 1940, 43, 188—194).—A review.

Potential use of hydrogen fluoride in organic chemical processes. J. H. SIMONS (Ind. Eng. Chem., 1940, 32, 178—183).—A review. R. S. C.

Nitric oxide-inhibited decomposition of *n*-butane.—See A., 1940, I, 167.

Decomposition and formation of organic peroxides.—See A., 1940, I, 168.

Oxidation of olefins derived from paraffins to fatty acids.—See B., 1940, 263.

1:2 and 1:4 addition. IV. Nitrogen tetroxide and isobutylene. V. Nitrogen tetroxide and tetramethylethylene. A. MICHAEL and G. H. CARLSON (J. Org. Chem., 1940, 5, 1—13, 14—23).—IV. In Et₂O there is no separation of the di-(α - β -nitrosonitric ester) of isobutane (I) (NO₂·O·CMe₂·CH₂·NO)₂ from the additive product derived from isobutene (II) and N₂O₄. Without solvent liquid (II) affords the di-(nitric ester) (III) in 7—12% yield; in light petroleum the yields vary more widely (0—13%) with similar experimental conditions. The course of the reaction does not vary appreciably with moderate changes in low temp.; the yields of (III) are 12% at -12° and 7.4% at -80°. N₂O₄ with (II) forms mainly gaseous products which have not been examined since extensive oxidation has occurred. Those formed in light petroleum decompose readily and cannot be separated into component parts. The liquid product formed in Et₂O is relatively stable and can be distilled under low pressure. The product obtained in light petroleum is transformed by NaSPh into a mixture of NaNO₃, NaNO₂, and an org. product which is oxidised to α -nitro- β -phenylsulphonylisobutane. Although the thio-ether corresponding with this sulphone is probably formed from α - β -dinitroisobutane (IV), this compound could not be isolated nor could the corresponding diamine be obtained by catalytic reduction of the crude or the distilled additive product formed in the light petroleum. NH₂Bu ^{β} is formed by catalytic reduction of the crude and the distilled additive product; this is probably formed mainly from nitroisobutene (V) and from (IV) through a series of reactions which also yield NHBu ^{β} ₂ (VI). NH₃ and β -hydroxyisobutylamine appear in practically equimol. proportion on reduction of the distilled blue oil; these products are probably derived from (I). Based on the yields of reduction products, (V) and (I) represent 5—12% and 16—23% respectively of the crude, additive product (VII). Assuming that the

isolated (VI) is formed from (IV), the latter constitutes at least 12% of (VII). The following appear new: α -nitro- β -phenylsulphonylisobutane, m.p. 89—90°; toluenesulphonyldiisobutylamide, m.p. 110—111°; isobutylamine *p*-nitrobenzoate, m.p. 117—128°; β -hydroxyisobutylamine *p*-nitrobenzoate, m.p. 137—138°; diisobutylamine camphorsulphonate, m.p. 185°; α -nitroso- β -phenylthiolisobutane, m.p. 86—87°.

V. The action of N₂O₄ on CMe₂:CMe₂ gives practically const. yields (19.6—22%) of β - γ -dinitro- β - γ -dimethylbutane (VIII) in Et₂O; addition of gaseous N₂O₄ to the alkene without solvent or in light petroleum gives only low yields of (VIII). β -Nitro- β - γ -dimethylbutan- γ -yl nitrate (IX) appears to be formed in variable amount under all the experimental conditions examined. In the absence of solvent and under strong oxidative conditions its yield is considerable. It readily unites with (VIII) to a double compound (X) in which all (VIII) is incorporated under the oxidising action of excess of N₂O₄. Accordingly (VIII) is isolated only under conditions tending to depress the oxidising action of N₂O₄ and the yield of (IX). The composition of (X) is deduced from the analytical data and from the relative amounts of the basic products [NH₃; NH₂·CMe₂·CMe₂·OH; (CH₂·NMe₂)₂] obtained by catalytic reduction. It is possible that N₂O₄ may oxidise CMe₂:CMe₂ to the corresponding oxide and then convert the latter into (IX). It is more probable that (IX) is formed by oxidation of the corresponding nitroso-nitric ester produced primarily by direct addition of N₂O₄ to the alkene. With the latter in excess and Et₂O as diluent, the yield of (VIII) is ~20%. This result in conjunction with the merging of (VIII) into (X) when an excess of N₂O₄ is used and the composition of (X) indicates that the crude reaction product, formed with approx. molar amounts of reactants, consists mainly of (VIII) and β -nitroso- β - γ -dimethylbutan- γ -yl nitrate and that the latter ester under the oxidising action of N₂O₄ is converted into (IX), which combines with (VIII) to yield (X). The results confirm those of Demjanov *et al.* (A., 1909, i, 754). In agreement, the occurrence of the dinitrite of Schmidt (A., 1903, i, 597) is not observed. Tetramethylethylenediamine di-*p*-nitrobenzoate, m.p. 213—214°, and β -amino- β - γ -dimethylbutan- γ -yl *p*-nitrobenzoate, m.p. 139°, appear new. H. W.

Hydrolysis and alcoholysis. W. HÜCKEL (Annalen, 1939, 540, 274—284; cf. A., 1939, II, 147; Ingold *et al.*, A., 1937, II, 363).—Substitution of Cl by OH during hydrolysis of *e.g.*, Bu ^{γ} Cl, CH₂PhCl, and CH₂:CH·CH₂Cl, is considered to involve addition of H₂O: R-Cl + HOH \rightarrow R- \ddot{C} :H-O-H; the C-Cl link-

ing is thereby polarised and facilitates separation of a hydrated Cl^- . The incomplete electron shell in SiCl_4 , PCl_5 , or BiCl_3 allows the formation of $\text{R}'\text{H} > \text{O} : \text{SiCl}_4$ etc. ($\text{R}' = \text{H}$ or Alk ; in the latter case, elimination of HCl or $\text{R}'\text{Cl}$ can occur). Hydrolysis of PCl_3 does not occur until H^+ and OH^- have been added (cf. NCl_3 where H.NCl_3 cannot add OH). RSO_2Cl give $\text{RSO}_2\text{Cl}:\text{HOH}$ and thence RSO_2 and $\text{Cl}:\text{HOH}$ but RCOCl undergo addition at the double linking. True substitution (type S_N2 ; Ingold) occurs only with difficultly hydrolysable chlorides. H. B.

Preparation of trimethylene bromide. Y. F. CHI and G. C. LIU (J. Chem. Eng. China, 1938, 5, 82).—The prep. from HBr and $\text{CH}_2:\text{CH}:\text{CH}_2\text{Br}$ is described. F. R. G.

Synthesis of $\gamma\gamma$ -dimethylpentan- β -ol. Y. F. CHI and C. H. SZA (J. Chem. Eng. China, 1938, 5, 62—64).—The Grignard compound from CMe_2EtBr and MeCHO yield $\gamma\gamma$ -dimethylpentan- β -ol, b.p. 152—157° (phthalate, m.p. 128—129°; *H* phthalate, m.p. 180—182°). F. R. G.

Reduction of tagetone to tagetol. T. G. H. JONES (Univ. Queensland Papers, 1939, 1, No. 11, 2 pp.).—Tagetone (A., 1926, 72) gives, by Ponnidoff reduction, tagetol, $\text{C}_{10}\text{H}_{18}\text{O}$, b.p. 55°/3 mm. (acetate, b.p. 65°/3 mm.). T. F. W.

Pyrolysis of higher fatty alcohols. H. GAULT, L. PALFRAY, and P. T. HSU (Compt. rend., 1939, 209, 999—1000).—Dodecanol with N_2 (100 kg. pressure) in the presence of Raney Ni (cf. A., 1936, 446) gives undecane (I), CO_2 , and CH_4 , which indicates that the reaction is one of pyrolysis. The yield of (I) increases with temp., time, and pressure of gas. At atm. pressure, besides (I), small amounts of lauraldehyde are formed, probably as an intermediate product in the reaction. J. L. D.

Synthesis of isopropyl ether. VII. Dehydration of isopropyl alcohol into isopropyl ether in the atmosphere of propylene under pressure, and supplementary experiments. M. KATUNO (J. Soc. Chem. Ind. Japan, 1939, 42, 422—424B; cf. A., 1938, II, 256).—The reactions between Pr^βOH and H_2SO_4 are: $\text{Pr}^\beta\text{OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{Pr}^\beta\text{O} \cdot \text{SO}_3\text{H}$ (I) + H_2O ; $\text{Pr}^\beta\text{OH} + (\text{I}) \rightleftharpoons \text{Pr}^\beta_2\text{O} + \text{H}_2\text{SO}_4$; (I) $\rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{SO}_4$. It is shown that if Pr^βOH and H_2SO_4 are heated in an agitating autoclave the third reaction can be almost completely prevented by the presence of added C_3H_6 under sufficient pressure. The yield of $\text{Pr}^\beta_2\text{O}$ reaches 62% of the theoretical. Increase in the proportion of H_2SO_4 beyond a certain val. decreases the yield of $\text{Pr}^\beta_2\text{O}$. H. W.

Tertiary oxonium salts. II. H. MEERWEIN, E. BATTENBERG, H. GOLD, E. PFEL, and G. WILLFANG (J. pr. Chem., 1939, [ii], 154, 83—156; cf. A., 1937, II, 46).—Numerous compounds, $[\text{R}_3\text{O}]^+\text{X}^-$, are prepared and proved to be true salts; they act as potent sources of R ions and thus take part in many characteristic reactions. Prep. of $[\text{Et}_3\text{O}]\text{BF}_4$, m.p. 92° (closed tube), from epichlorohydrin (I) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in Et_2O is improved to give a quant. yield. Use of $\text{BF}_3 \cdot \text{Pr}^\beta_2\text{O}$ in $\text{Pr}^\beta_2\text{O}$ gives only 30% of tri-*n*-

propyloxonium borofluoride, m.p. 73—74° (decomp.), the reaction being: $(\text{I}) + 4\text{BF}_3 \cdot \text{R}_2\text{O} + 2\text{R}_2\text{O} \rightarrow 3[\text{R}_3\text{O}]\text{BF}_4 + \text{B}\{\text{O} \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OR}\}_3$. Etherates of SbCl_5 , FeCl_3 , and AlCl_3 also give oxonium salts, reacting with (I) and, often, $(\text{CH}_3)_2\text{O}$ according to the equation (A) $(\text{CH}_3)_2\text{O} + 2\text{MCl}_n \cdot \text{R}_2\text{O} \rightarrow [\text{R}_3\text{O}]\text{MCl}_{n+1} + \text{OR} \cdot [\text{CH}_2]_2 \cdot \text{OMCl}_{n-1}$. The salts are pptd. during the reaction; the alkoxychlorides are recovered from the mother-liquors. Thus are obtained trimethyloxonium antimonihexachloride (95.5%), m.p. 158° (decomp.; sinters at 156°), and triethyloxonium antimonihexachloride (II) (95%) [prep. from (I) or $(\text{CH}_3)_2\text{O}$], m.p. 135—137° (decomp.), aluminotrichloride (82%), m.p. 72° (decomp.), and ferritetrachloride (100%), m.p. 74° (decomp.), *Sb* β -chloro- β' -ethoxyisopropoxytetrachloride, $\text{SbCl}_4 \cdot \text{O} \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OEt}$ (III), m.p. 91°, and *Al*, m.p. (crude) 114—115°, and *Fe* β -chloro- β' -ethoxyisopropoxydichloride, m.p. (crude) 103—105°. $\text{SbCl}_4 \cdot \text{O} \cdot [\text{CH}_2]_2 \cdot \text{OEt}$ and $\text{SbCl}_4 \cdot \text{O} \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OMe}$ are obtained only as oils, their structures being proved by hydrolysis by neutral, aq. Seignette salt-KOH to $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{OEt}$ and γ -chloro- α -methoxy-*n*-propan- β -ol, b.p. 170—174° [rapidly converted by cold 0.1*N*-NaOH into (I)], respectively; the structure of the cryst. *Sb* and *Al* alkoxyhalides is similarly proved by hydrolysis to $\text{OH} \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OEt}$ (IV), b.p. 178—184°/760 mm., 71—73°/13 mm. $\text{BF}_3 \cdot \text{R}_2\text{O}$ ($\text{R} = \text{Me}$ or Et) and MeF at room temp. give trimethyl-, m.p. 148° (decomp.) (cautious heating regenerates $\text{BF}_3 \cdot \text{Me}_2\text{O}$ and MeF), and methyldiethyloxonium borofluoride, m.p. 99—100° (decomp.) (cf. *loc. cit.*). Similarly $\text{SbCl}_5 \cdot \text{Et}_2\text{O}$ (prep. at -80°), m.p. 88°, and EtCl at room temp. (1 week) give (II). Attempts to add (a) MeCl or EtCl to etherates of AlCl_3 , FeCl_3 , BCl_3 , and SnCl_4 , and (b) $\text{SbCl}_5 \cdot \text{Et}_2\text{O}$ to $\text{CH}_2\text{Cl} \cdot \text{OMe}$ (gives CH_2O and MeCl), CH_2PhCl (gives HCl and tars), or AcCl (gives EtOAc and EtCl), failed. It follows that addition of AlkCl plays no part in reaction (A), the mechanism of which is elucidated mainly by analogous reactions in the N-series. $\text{BF}_3 \cdot \text{C}_5\text{H}_5\text{N}$ with $(\text{CH}_3)_2\text{O}$ or (I) at 0° gives the betaines, $\text{C}_5\text{H}_5\text{N}^+[\text{CH}_2]_2 \cdot \text{O} \cdot \text{BF}_3^-$ (V), m.p. 131—132°, and $\text{C}_5\text{H}_5\text{N}^+ \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{O} \cdot \text{BF}_3^-$, m.p. 164—165°, respectively; $\text{BF}_3 \cdot \text{NMe}_3$ and $(\text{CH}_3)_2\text{O}$, first at 40—45° and then at 65—70°, give the betaine, $^+\text{NMe}_3 \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot \text{BF}_3^-$, m.p. 296—298°. The salt structure of these products is proved by solubility in MeNO_2 , liquid SO_2 , and H_2O (to give initially neutral solutions), insolubility in most org. solvents, and by conversion of (V) by aq. NaHgI_3 into 1- β -hydroxyethylpyridinium mercuritri-iodide, m.p. 39°, and by NaHgCl_3 into $[\text{C}_5\text{H}_5\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}]\text{Cl} \cdot 6\text{HgCl}_2$. Similarly $\text{SbCl}_5 \cdot \text{Et}_2\text{O}$ with (I) or $(\text{CH}_3)_2\text{O}$ in Et_2O at -80° gives the betaines, $\text{SbCl}_5 \cdot \text{O} \cdot \text{CH}(\text{CH}_2\text{Cl}) \cdot \text{CH}_2 \cdot \text{OEt}_2^+$ (VI), decomp. 58°, and $\text{SbCl}_5 \cdot \text{O} \cdot [\text{CH}_2]_2 \cdot \text{OEt}_2^+$ (VI), decomp. 58°. These salts are very unstable; in moist air they give the appropriate glycol Et ether and EtOH ; in absence of H_2O at room temp. to 90° they give quantitatively EtCl with (III) and *Sb* β -ethoxyethoxytetrachloride (VIII), m.p. 106°, respectively. The EtCl thus formed is set free as Et^+ and Cl^- , and

it is this fission which leads to formation of $[R_3O]X$. In confirmation of this, it is shown that $SbCl_5 \cdot Et_2O$ with (VI) or (VII) in Et_2O gives quantitatively $[Et_3O]SbCl_6$ with (III) or (VIII), respectively; these reactions are rapid although all the reagents and products are insol. in Et_2O . $BF_3 \cdot Me_2O$ and (I) in Et_2O at -80° give the *betaine*,

$BF_3 \cdot O \cdot CH(CH_2Cl) \cdot CH_2 \cdot OMe_2$, m.p. $75-80^\circ$ (decomp.), which very rapidly decomposes to BF_3 and an oil. $BF_3 \cdot Et_2O$ and (I) at -80° give a similar *betaine*, which with a second mol. of $BF_3 \cdot Et_2O$ gives $[Et_3O]BF_4$ and $OEt \cdot CH_2 \cdot CH(CH_2Cl) \cdot O \cdot BF_2$; the BF_2 ester is not isolated, as it disproportionates at once to 2 BF_3 and $\{OEt \cdot CH_2 \cdot CH(CH_2Cl) \cdot O\}_2B$ (IX), b.p. $146-151^\circ/0.05$ mm. Decomp. of the last-mentioned *betaine* in Et_2O at room temp. gives $[Et_3O]BF_4$, $BF_3 \cdot Et_2O$, and the BF_3 compound of (IV), with small amounts of (IX) and γ -chloropropylene glycol *Et_2* ether (X), b.p. $72-73^\circ/14$ mm. Reaction (A) thus occurs by formation of a *betaine* and reaction thereof with a second mol. of inorg. halide etherate; these two steps are often manifested by physical changes in the reaction mixture.

Various other inorg. halides do not give simple oxonium salts. $SnCl_4$ and (I) in Et_2O give the cryst., double *betaine*, $\bar{S}nCl_4 \cdot \{O \cdot CH(CH_2Cl) \cdot CH_2 \cdot OEt\}_2$, which is very unstable, giving by hydrolysis $EtOH$, (IV), and (X), or by decomp. at room temp. (a) $2EtCl + SnCl_4 \cdot \{O \cdot CH(CH_2Cl) \cdot CH_2 \cdot OEt\}_2$, (b) by interaction with 2 Et_2O , $2(X) + SnCl_4 \cdot 2Et_2O$, and (c) a small amount of the cryst. compound, $(CH_2Cl)_2CH \cdot O \cdot SnCl_3$, hydrolysed mainly to $OH \cdot CH(CH_2Cl)_2$, b.p. $69-71^\circ/13$ mm. (identified as phenylurethane, m.p. $73-74^\circ$). $BeCl_2 \cdot Et_2O$, an oil, and (I) in Et_2O give *Be* $\beta\beta'$ -*dichloroisopropoxychloride*, $(CH_2Cl)_2CH \cdot O \cdot BeCl$, + Et_2O , m.p. $114.5-115^\circ$, the structure of which is shown by removal of 1 Cl by $AgNO_3$ -dil. HNO_3 , 2 Cl by $2N-NaOH$ (gives *epi*-chlorohydrin), and 3 Cl by boiling $0.5N-KOH-BuOH$; hydrolysis gives $OH \cdot CH(CH_2Cl)_2$. $BeCl_2$ and $(CH_2)_2O$ in Et_2O similarly give *Be* β -*chloroethoxychloride*, + Et_2O (not lost even at 200°), m.p. $199-200^\circ$. $BiCl_3$ and (I) in Et_2O or C_6H_6 give *Bi* $\beta\beta'$ -*dichloroisopropoxydichloride*, m.p. $145-150^\circ$ (decomp.) [hydrolysed to $OH \cdot CH(CH_2Cl)_2$]. These three products are

formed by the reaction: $CHR' \cdot CH_2 \cdot O + MCl_n \cdot R_2O \rightarrow CH_2Cl \cdot CHR' \cdot O \cdot MCl_{n-1} + R_2O$ ($R' = H$ or CH_2Cl). $ZnCl_2$, BCl_3 , $AlBr_3$, $TiCl_4$, and $SbCl_5$ react in the main similarly; the products from $ZnCl_2$ and BCl_3 are insol. oils, those from the remainder are sol., but in all cases hydrolysis to $OH \cdot CH(CH_2Cl)_2$ proves the nature of the reaction [$AlBr_3$ gives a product, hydrolysed to $CH_2Cl \cdot CH(OH) \cdot CH_2Br$]; about 30% of (IV) is also formed by hydrolysis, so that the reaction, $(I) + MCl_n \cdot Et_2O \rightarrow OEt \cdot CH_2 \cdot CH(CH_2Cl) \cdot O \cdot MCl_{n-1} + EtCl$, also occurs. SiF_4 forms no etherate, is insol. in Et_2O , and does not react with (I).

The salt character of the oxonium compounds is proved by solubility in liquid SO_2 and $MeNO_2$, sometimes (less so) in $PhNO_2$, CH_2Cl_2 , or $CHMeCl_2$, insolubility in other org. solvents, particularly Et_2O , and by their conductivity in liquid SO_2 , which is intermediate between that of KI and NMe_4I and

approx. equal to that of $SEt_3 \cdot BF_4$. The conductivity of $[Me_3O]BF_4$ is $<$ that of $[Et_3O]BF_4$ owing to different degrees of solvation. The outstanding property of the salts is their power of alkylation by transference of Alk^+ . Thermal decomp. gives RCl and R_2O . A reversible reaction, $[R_3O]^+ + R'_2O \rightleftharpoons R_2O + [RR'_2O]^+$, is realised by using an excess of either ether or otherwise suitable conditions. Thus, $[Et_3O]BF_4$ is completely (92%) converted into $[Me_3O]BF_4$, m.p. 143° , by Me_2O in 5 days at room temp., the conversion being favoured by the lower solubility of the latter salt. This reaction occurs also with cyclic ethers and can be brought nearly to completion by removing the liberated lower ether in vac.; thus are obtained *pentamethylene-ethyloxonium*

borofluoride (XI), $[Et \cdot O \cdot \langle \begin{smallmatrix} [CH_2]_2 \\ [CH_2]_2 \end{smallmatrix} \rangle \cdot CH_2]BF_4$ (from pyran and $[Et_3O]BF_4$), m.p. 45° , hygroscopic, *tetra-methylene-ethyl-* (XII), m.p. 132° (decomp.), $\alpha\alpha'$ -*dimethyltetramethylene-ethyl-* (XIII),

$[Et \cdot O \cdot \langle \begin{smallmatrix} CHMe \cdot CH_2 \\ CHMe \cdot CH_2 \end{smallmatrix} \rangle]SbCl_6$, m.p. 142° (decomp.), and *pentamethylene-ethyl-*, m.p. $154-155^\circ$ (decomp.), *-oxonium antimonihexachloride*, and the salt [from dioxan in $(CH_2Cl)_2$], $[O \cdot \langle \begin{smallmatrix} [CH_2]_2 \\ [CH_2]_2 \end{smallmatrix} \rangle \cdot O \cdot Et]SbCl_6$, m.p.

156° (decomp.). (A similar interchange accounts for formation of $[Me_3O]BF_4$ as sole product from $BF_3 \cdot Me_2O$ and Pr^aF .) No reaction, however, occurs between $[Et_3O]$ salts and Pr^b_2O or cineole, in spite of the high basicity of these ethers evidenced by solubility in H_2O and HCl ; this is ascribed to steric hindrance around the O; in the case of (XIII), hindrance is reduced by ring-formation. Crowding around the O similarly accounts for Alk_3O salts being less stable than are Alk_3S salts; this difference disappears when Alk is replaced by the smaller H, so that ethers, but not sulphides, form salts of the type, $[R_2HO]X$, with acids. The tendency to lose Alk^+ leads to ready hydrolysis of $[R_3O]BF_4$ by H_2O to R_2O , HBf_4 , and ROH , this reaction being in effect alkylation of H_2O or OH^- . $[Et_3O]FeCl_4$ behaves similarly. However, $[Et_3O]AlCl_4$ in H_2O gives Et_2O , $AlCl_3$, and $EtCl$; hydrolysis to $EtOH$ occurs only in $2N-NaOH$; the difference is due to instability of $AlCl_4^-$ in H_2O , which leads to immediate decomp. of the salt to $[Et_3O]Cl$ and hydrolysis products of $AlCl_3$; the $EtCl$ is derived by the secondary decomp. of $[Et_3O]Cl$. $[R_3O]SbCl_6$ occupies an intermediate position, dil. alkali giving both RCl and ROH . Hydrolysis of (XII) by $2N-NaOH$ takes both possible routes, viz., formation of varying amounts of (a) $EtOH$ and tetrahydrofuran, and (b) $OEt \cdot [CH_2]_4 \cdot OH$ (XIV), b.p. $87^\circ/19.5$ mm.; some *di-8-ethoxy-n-butyl ether*, b.p. $140^\circ/18.5$ mm., is also formed by interaction of (XIV) with unchanged (XII). Reaction (b) is the counterpart (at room temp.) of Hofmann fission of $NR_4 \cdot OH$. Hydrolysis of $[R_3O]BF_4$ by H_2O is not instantaneous and is followed by (a) the increasing conductivity due to liberated HBf_4 (which decomposes relatively slowly) and (b) pptn. of unchanged salt by $NaHgI_3$. The two methods give similar results, e.g., in $0.0528N$ solution at 18° decomp. times are $R = Me$ 8, Et 80, Pr^a 120, and (XI) 220 min.; these figures represent the relative ease of

removal of Alk^+ . By treating $[\text{Et}_3\text{O}]\text{BF}_4$ with 1 equiv. of NaOH , measuring the rate of increase of conductivity, and extrapolating to zero time, $[\text{Et}_3\text{O}]\text{OH}$ is shown to have $\Delta_\infty \sim 200$ at 20° , indicating a strength as base comparable with that of $\text{NEt}_4\cdot\text{OH}$ (211.5 at 25°) and $\text{SEt}_3\cdot\text{OH}$ (215.8 at 25°). By virtue of this temporary stability in H_2O , double decomp. of oxonium and inorg. salts (or acids) leads to new oxonium salts. *E.g.*, $[\text{Me}_3\text{O}]\text{BF}_4$ and 10% aq. HAuCl_4 give *trimethyloxonium aurichloride*, $[\text{Me}_3\text{O}]\text{AuCl}_4$, m.p. 133° (decomp.), and the following salts are similarly prepared (those marked * are not described in detail): $[\text{Et}_3\text{O}]\text{AuCl}_4$, m.p. 92° (decomp.), $[\text{Et}_3\text{O}]_2\text{PtCl}_6$, decomp. $>120^\circ$, $[\text{Et}_3\text{O}]\text{SbCl}_6$ (cf. above), $[\text{Et}_3\text{O}]_2\text{SnCl}_6$, unstable at room temp., m.p. indefinite, $[\text{Et}_3\text{O}]\text{BiI}_4$ (obtained by NaBiI_4 at $<0^\circ$), bright red, $[\text{Et}_3\text{O}]\text{BiI}_7$ (obtained by NaBiI_4 at 0°), dark red (loses EtI at room temp. or rapidly at 60°), $[\text{Et}_3\text{O}]\text{BiCl}_7$ (from NaBiCl_4), m.p. 84° (decomp.), $[\text{Et}_3\text{O}]\text{HgI}_3$, cryst. (at room temp. or rapidly at 50 – 60° gives Et_3O and EtI), $[\text{Et}_3\text{O}]\text{HgCl}_3$, $[\text{Et}_3\text{O}]_2\text{H}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ [from acidified $\text{Na}_4\text{Fe}(\text{CN})_6$], unstable, the *aurichloride* and *mercuritriiodide** from (XI), $[\text{Me}_3\text{O}]_2\text{PtCl}_6^*$, $[\text{Me}_3\text{O}]_2\text{SbCl}_6^*$, $[\text{Me}_3\text{O}]\text{BiI}_7^*$, $[\text{Me}_3\text{O}]\text{HgI}_3^*$, and $[\text{Me}_2\text{EtO}]\text{AuCl}_4^*$. HHgCl_3 , HHgBr_3 , and HCdI_3 give insol., but unstable, ppts. HClO_4 and H_2SnCl_6 give no salts. Reinecke's salt gives esters in place of oxonium salts. The stability of these salts varies widely. That of the mercuritriiodides parallels the rates of hydrolysis reported above. Addition of $[\text{R}_3\text{O}]\text{BF}_4$ to aq. NaX causes (if $[\text{R}_3\text{O}]\text{X}$ is sol.) (a) hydrolysis as described above and (b) alkylation of the anion, thus: $[\text{R}_3\text{O}]^+ + \text{X}^- \rightarrow \text{R}_2\text{O} + \text{RX}$; determination of the amount of acid liberated by hydrolysis shows the following % of reaction (b): F a trace, Cl 12, Br 23, I 53, CNS 64, CN 55. Alkylation of X is largely dependent on the polarisability of the anion (CN^- behaving abnormally owing to alkalinity of aq. cyanides). This factor and steric conditions around the O largely determine the stability of oxonium salts. The stability series for anions, $\text{SbCl}_6 > \text{BF}_4 > \text{FeCl}_4 > \text{AlCl}_4 > \text{SnCl}_6$, holds for all onium salts. The alkylating action of oxonium salts on other org. compounds (cf. *loc. cit.*) is very powerful. $[\text{Et}_3\text{O}]\text{BF}_4$ with Et_2SO , m.p. 13 – 14° (lit. 5 – 6° , 15°), b.p. $90^\circ/15$ mm., gives *ethoxydiethylsulphonium borofluoride*, $[\text{Et}_2\text{S}\cdot\text{OEt}]\text{BF}_4$; the corresponding antimonihexachloride is obtained from $[\text{Et}_3\text{O}]\text{SbCl}_6$; both products are unstable. NMe_3O in CH_2Cl_2 similarly gives *ethoxytrimethylammonium borofluoride*, $[\text{NMe}_3\cdot\text{OEt}]\text{BF}_4$, and antimonihexachloride. $\text{CO}(\text{NH}_2)_2$ and $[\text{Et}_3\text{O}]\text{BF}_4$ (no solvent) give the salt, $[(\text{NH}_2)_2\text{C}\cdot\text{OEt}]\text{BF}_4$ (or similar mesomeric form), m.p. 184 – 185° (decomp.), converted by cold, conc. NaOH into $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{OEt}$. NH_2Ac gives similarly the salt, $[\text{NH}\cdot\text{CMe}\cdot\text{OEt}]\text{BF}_4$. $[\text{Et}_3\text{O}]\text{AlCl}_4$ and PhCN give a salt, $[\text{CPh}:\text{NEt}]\text{AlCl}_4$, which with a further mol. of PhCN gives $\text{CPhCl}:\text{NEt}$ (recognised by hydrolysis to $\text{NH}\cdot\text{EtBz}$) and the compound, $\text{PhCN}\cdot\text{AlCl}_3$, m.p. 96 – 98° . Alkylation of other nitriles, saturated and unsaturated ketones is mentioned. The following observations are also recorded. A compound, $\text{B}(\text{O}[\text{CH}_2]_2\cdot\text{Cl})_3\cdot 2\text{BF}_3$, is obtained; it loses all the BF_3 readily and does not give a borofluoride; $\text{B}(\text{OPh})_3$ behaves similarly. The

stability of salts, $[\text{R}_2\text{HO}]\text{X}$, generally parallels that of $[\text{R}_3\text{O}]\text{X}$, but $[\text{R}_2\text{HO}]\text{BF}_4$ and $[\text{R}_2\text{HO}]\text{SbCl}_6$ are unexpectedly unobtainable. BF_3 compounds are readily analysed by pptn. of PbClF by PbCl_2 , but BF_4 salts react too slowly with PbCl_2 and are best determined by nitron. R. S. C.

Preparation, properties, and thiocyanogen absorption of triolein and trilinolein. D. H. WHEELER, R. W. RIEMENSCHNEIDER, and C. E. SANDO (J. Biol. Chem., 1940, **132**, 687–699).—Oleic acid ($>0.1\%$ of saturated acids and linoleic acid), glycerol, and 1% of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ at 125° in N_2 evolve H_2O and give triolein (I), which is purified by mol. distillation. Cooling and warming curves show that (I) exists in 3 forms: *form I*, stable, m.p. 4.7 – 5.0° ; *form II*, m.p. $\sim -12^\circ$; and *form III*, m.p. $\sim -32^\circ$. Linoleic acid similarly gives trilinolein (II), which gives *form I*, stable, m.p. -13.1° to -12.8° , and *form II*, m.p. $\sim -43^\circ$. CNS vals. for (I) and (II) at 20 – 23° are determined after various periods; the best reaction time for determinations, especially in mixtures of (I) and (II), is 4 hr. With Br in cold Et_2O , (II) gives a mixed product, with a 9.1% yield of cryst. Br-compounds, m.p. 80 – 81° and 81 – 81.7° . E. W. W.

Synthesis of phosphoric esters. I. P. BRIGL and H. MÜLLER (Ber., 1939, **72**, [B], 2121–2130).— $(\text{OPh})_2\text{POCl}$ (I) is best obtained by heating equal parts by wt. of PhOH and POCl_3 slowly to 180° and then, after subsidence of the first marked evolution of HCl , to 225° and subsequently for a short time at 260° . It is separated from simultaneously formed $(\text{OPh})\text{POCl}_2$ by fractional distillation and has b.p. 191 – $194^\circ/12$ mm. It is converted by cold $2\text{N}\cdot\text{NaOH}$ into $(\text{OPh})_2\text{PO}\cdot\text{OH}$, which suffers hydrogenating fission (PtO_2 in AcOH) to H_3PO_4 and cyclohexane. Gradual addition of (I) to $\alpha\beta$ -isopropylideneglycerol in $\text{C}_5\text{H}_5\text{N}$ or quinoline at 0° and then at room temp. yields *Ph₂ $\alpha\beta$ -isopropylidene- α' -glyceryl phosphate*, which does not crystallise and cannot be distilled unchanged in a high vac. It undergoes hydrogenating fission to α -glycerylphosphoric acid (II) (isolated as the Ba salt): more simply it is hydrolysed to (II), COMe_2 , and PhOH by the prolonged action of aq. AcOH at 40 – 45° . Similarly, $\alpha\alpha'$ -benzylideneglycerol, m.p. 84° , is converted into *Ph₂ $\alpha\alpha'$ -benzylidene- β -glyceryl phosphate*, m.p. 72.5° , which is hydrolysed by 65% AcOH at 45 – 50° to β -glycerylphosphoric acid [*Ba* ($+1\text{H}_2\text{O}$) salt]; hydrogenation gives only a small amount of the latter compound since the Ph residues appear to be eliminated whereas the CHPh : residue is mainly hydrogenated. 2:3:4:5-Diisopropylidene-fructose is transformed into *Ph₂ 2:3:4:5-diisopropylidene-fructose 1-phosphate*, m.p. 52.5° , $[\alpha]_D^{20} -29.1^\circ$ in COMe_2 , catalytically hydrogenated to 2:3:4:5-diisopropylidene-fructose-1-phosphoric acid, isolated as the Ba salt ($+3\text{H}_2\text{O}$). *Ph₂ 1:2:4:5-diisopropylidene-fructose 3-phosphate* (III), m.p. 71 – 72° , $[\alpha]_D^{20} -124.9^\circ$ in COMe_2 , is slowly converted by 70% AcOH at room temp. into *Ph₂ 1:2-isopropylidene-fructose 3-phosphate*, m.p. 136° , $[\alpha]_D^{20} -84.5^\circ$ ($c = 2.792$) or -96.4° ($c = 2.133$) in COMe_2 , which is very stable towards further action of AcOH and is reconverted by $\text{CuSO}_4\text{-COMe}_2$ into (III). Hydro-

generating fission leads to 1:2-isopropylidene-fructose-3-phosphoric acid [$\text{Ba} (+2\text{H}_2\text{O})$ salt], hydrolysed by 0.1N- H_2SO_4 to COMe_2 and fructose-3-phosphoric acid. 2:3-iso-propylidene-fructofuranose affords Ph_4 2:3-isopropylidene-fructofuranose diphosphate, $\text{C}_{33}\text{H}_{34}\text{O}_{12}\text{P}_2$, m.p. 120.5° , $[\alpha]_D^{20} +12.4^\circ$ in COMe_2 , which is stable towards 65% AcOH at room temp. and at 40° and, when hydrogenated, gives mainly a fructosemonophosphoric acid which can contain only a very small proportion of diphosphoric acid. Fructofuranose 1:6-dibenzoate is transformed by PhCHO and ZnCl_2 into 2:3(or 2:4)-benzylidene-fructofuranose 1:6-dibenzoate, dimorphous, m.p. 85° (from C_6H_6) or $102\text{--}103^\circ$ (from MeOH or AcOH by addition of H_2O), $[\alpha]_D +26^\circ$ to $+28^\circ$ in COMe_2 . This is hydrogenated (PtO_2) in MeOH containing H_3PO_4 to a substance, $\text{C}_{27}\text{H}_{42}\text{O}_8$, m.p. 82° , which is without action on Fehling's solution, and ($\text{Pd}\text{--}\text{BaSO}_4$) in MeOH containing H_3PO_4 to fructose 1:6-dibenzoate.

H. W.

Isolation and properties of *R*-diphosphoglyceric acid. E. NEGELEIN and H. BRÖMEL (Biochem. Z., 1939, 303, 132—144; cf. A., 1939, III, 788).—The labile glyceric acid diphosphate, probably $\text{PO}_3\text{H}_2\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{PO}_3\text{H}_2$ (*R*-acid) (I), now named *R*-diphosphoglyceric acid, is obtained in 57% yield by the interaction of β -phosphoglyceraldehyde (II), inorg. PO_4''' , a small amount of diphosphopyridine nucleotide, MeCHO , and the cryst. proteins of the carbohydrate-oxidising enzyme and MeCHO reductase at p_H 7.6. The p_H of the mixture is adjusted to 2.1 with H_2SO_4 and the H salt of (I) is pptd. by adding 10 vols. of COMe_2 . The ppt., dissolved in H_2O and treated with neutralised solution of strychnine hydrochloride, yields the tetrastrychnine salt of (I). (I) has an absorption band at 215 μ . It is detected and determined by adding excess of dihydropyridine nucleotide (III) to a solution of (I) free from inorg. PO_4''' and measuring the decrease in ultra-violet light absorption resulting from the oxidation of an equiv. amount of the nucleotide. In neutral aq. solution at 38° (I) spontaneously decomposes at the rate of 2.6% per min. thus: $(\text{I}) + \text{H}_2\text{O} = 3\text{-phosphoglyceric acid} + \text{H}_3\text{PO}_4$. (I) contains an asymmetric C ($[\alpha]$ very small) since the phosphoglyceric acid produced in the spontaneous decomp. has $[\alpha]_D^{20} -675^\circ$ in 8% NH_4 molybdate solution. The reactions involved in the production of (I) are: $(\text{II}) + \text{PO}_4''' + \text{pyridine nucleotide (IV)} \rightleftharpoons (\text{I}) + (\text{III})$ and $(\text{III}) + \text{MeCHO} \rightleftharpoons (\text{IV}) + \text{EtOH}$, the first reaction being catalysed by the carbohydrate-oxidising enzyme and the second by MeCHO reductase.

W. McC.

Action of thionyl chloride and thionyl bromide on pentaerythritol. F. GOVAERT and M. HAUSEUS (Natuurwetensch. Tijds., 1939, 21, 215—217).—Pentaerythritol disulphite, m.p. 151° , is formed by interaction of $\text{C}(\text{CH}_2\cdot\text{OH})_4$ and SOCl_2 or SOBr_2 alone or in presence of a *tert.* base. SOBr_2 and the appropriate alcohol gives the corresponding bromide (yield given in parentheses): *iso*amyl (80), *sec.*-octyl (73), *Bu* ^{γ} (55), and CH_2Ph (70%). S. C.

Action of Nessler's reagent on dichloroethyl sulphide (Yperite) and β -chlorovinylchloro-

arsines (Lewisite) in aqueous medium. J. DELGA (J. Pharm. Chim., 1940, [ix], 1, 5—8).—Presence of $(\text{Cl}\cdot[\text{CH}_2]_2)_2\text{S}$ (I) or of Lewisite (II) in H_2O hinders the use of Nessler's reagent for NH_3 , (I) giving a white ppt. [not formed by $(\text{OH}\cdot[\text{CH}_2]_2)_2\text{S}$], and (II), in increasingly conc. solutions, in turn a greenish-yellow colour, an orange-yellow or maroon colour, a grey ppt., and a white ppt. turning grey. The use of these reactions for detecting (I) and (II) is suggested. E. W. W.

Reaction between $\beta\beta'$ -dichlorodiethyl sulphide (mustard gas) and bleaching powder. A. G. LIPSCOMBE (Analyst, 1940, 65, 100).—Dry CaOCl_2 does not appear to react with mustard gas, but on addition of a few drops of H_2O a violent reaction takes place. E. C. B. S.

Thiodiglycol. Unit process and operations involved in its synthesis from ethylene oxide and hydrogen sulphide. D. F. OTHMER and D. Q. KERN (Ind. Eng. Chem., 1940, 32, 160—169).—The change, $2(\text{CH}_2)_2\text{O} + \text{H}_2\text{S} \rightarrow \text{S}[(\text{CH}_2)_2\cdot\text{OH}]_2$, occurs in the liquid reaction product only, is a third-order reaction, and gives >99% yield. Admission of the gases and withdrawal of the product from the reaction vessel may be continuous. R. S. C.

Sulphur studies. XV. Synthesis of alkane-sulphonic acids and certain derivatives. P. H. LATIMER and R. W. BOST (J. Org. Chem., 1940, 5, 24—28).—The alkyl halide (I) and aq. $(\text{NH}_4)_2\text{SO}_3$ are heated on the steam-bath for 3—4 hr. at a temp. just below the refluxing point of (I), after which the mixture is gently refluxed for 30—40 hr. The mixture is diluted and boiled with $\text{Ba}(\text{OH})_2$ until NH_3 is no longer evolved. BaSO_3 is removed and excess of $\text{Ba}(\text{OH})_2$ is pptd. by CO_2 . The dry mixture of *Ba* halide and *Ba* methane- (II), ethane- (III), and *n*-propane- (IV) -sulphonate is continuously extracted with abs. EtOH to remove the halide and finally crystallised from 80% EtOH . *Ba n*-butane- (V), *n*-pentane- (VI), *n*-hexane- (VII), and *n*-heptane- (VIII) -sulphonates separate from the filtrate on concn. and are purified from the last traces of halide by fractional crystallisation from distilled H_2O . (II)—(VIII) are transformed into the corresponding phenylhydrazonium salts, m.p. $193\text{--}194^\circ$ (decomp.), 182.8° , 204.5° (decomp.), $114\text{--}115^\circ$, $108\text{--}108.2^\circ$, $101\text{--}101.6^\circ$, and $100\text{--}100.5^\circ$, respectively. (II)—(VI) yield the corresponding *p*-toluidides, m.p. $102.0\text{--}102.7^\circ$, $80.0\text{--}80.5^\circ$, $67.0\text{--}67.8^\circ$, $74.2\text{--}75.2^\circ$, and $48.4\text{--}49.4^\circ$, and *p*-phenetidides, m.p. $126.5\text{--}127.4^\circ$, $80.4\text{--}81^\circ$, $101.0\text{--}101.5^\circ$, $78.2\text{--}79.0^\circ$, and $69.0\text{--}70.0^\circ$, respectively. *o*-Benzylorxyphenyl, m.p. $92\text{--}93^\circ$, and β -naphthyl, m.p. $103.5\text{--}104.5^\circ$, methanesulphonate are described. The *n*-alkanesulphonyl-*p*-phenetidides and -*p*-toluidides afford no protection to mice infected with pneumococcus type I, type II, Puerto Rican strain, influenza virus, or staphylococcus. Methanesulphonyl-*p*-toluidide shows antipyretic action which is not const. between rats and rabbits. H. W.

Formic acid as a solvent for ozonisation investigations. R. M. DORLAND and H. HIBBERT (Canad. J. Res., 1940, 18, B, 30—34).—Comparison of the actions of O_3 on maleic acid (I), vanillin (II),

and veratraldehyde (III), in HCO_2H (IV) and in EtOAc (V), shows that in (IV), (I) affords $\text{CHO}\cdot\text{CO}_2\text{H}$ whilst (II) and (III) are unchanged, whereas in (V), (I) affords mainly $\text{H}_2\text{C}_2\text{O}_4$, (II) vanillic acid, and (III) veratric acid. The effect of (IV) in protecting CHO is noteworthy. F. J. G.

Physical properties of aliphatic acid anhydrides.—See A., 1940, I, 149.

Electrolysis [of sodium acetate, potassium hexoate, and potassium ethyl malonate] in the glow discharge.—See A., 1940, I, 169.

Addition of hydrogen bromide to non-terminal double bonds. The isopropylidene group. Crotonic acid. D. C. GRIMSHAW, J. B. GUY, and J. C. SMITH (J.C.S., 1940, 68—71).—Addition of HBr to $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in C_6H_6 even under the most favourable peroxidic conditions with Bz_2O_2 , BzO_2H , or ascaridole gave only $\text{CEtBr}\cdot\text{CO}_2\text{H}$. Et_2 α -acetyl-brassyate hydrolysed with KOH in EtOH yields μ -ketotetradecoic acid, m.p. 75° (*Et* ester, b.p. $153^\circ/0.5$ mm., m.p. 36°), which with MgMeI gives μ -hydroxy- μ -methyltetradecoic acid, m.p. 61° . $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_{15}\cdot\text{Me}$ is shown to contain the CMe_2 group by ozonolysis to $\text{Me}\cdot[\text{CH}_2]_{15}\cdot\text{CO}_2\text{H}$, whilst addition of HBr gives solely β -bromo- β -methyl-nonadecane (I), m.p. 19.4° , also prepared from $\text{C}_{17}\text{H}_{35}\cdot\text{CMe}_2\cdot\text{OH}$ and HBr. $\text{C}_{17}\text{H}_{35}\text{I}$ in PhMe reacts with $\text{CHNa}(\text{CO}_2\text{Et})_2$ to give Et_2 heptadecylmalonate, b.p. $198\text{--}202^\circ/0.4$ mm., m.p. 20° and $32\text{--}33^\circ$, which with MeI yields Et_2 methylheptadecylmalonate, b.p. $195\text{--}197^\circ/0.5$ mm., m.p. 11° and 25° , hydrolysed with aq. KOH to methylheptadecylmalonic acid, m.p. $100\text{--}101^\circ$; this loses CO_2 on heating to give α -methylnonadecoic acid, m.p. 57.5° , f.p. 56.4° , the *Et* ester, b.p. $170^\circ/0.12$ mm., of which is reduced with Na in EtOH to β -methylnonadecan- α -ol, b.p. $167^\circ/0.2$ mm., m.p. $39\text{--}40^\circ$. This compound with HBr at $130\text{--}150^\circ$ or with PBr_5 gives α -bromo- β -methylnonadecane (II), m.p. 14.1° and 16.5° , f.p. 14.0° . M.p. are recorded for mixtures of (I) and (II). F. R. G.

Polarographic study of pentenoic acids. V. ZAMBOTTI (Arch. Sci. biol., Napoli, 1940, 26, 80—88).—There appears to be no polarographic difference in the properties of the double linking in the $\alpha\beta$, $\beta\gamma$, or $\gamma\delta$ positions in the *n*-pentenoic acids. The biological activity of the $\alpha\beta$ double linking must be referred not to the substrate but to the influence of enzymes.

S. O.

Racemisation of carboxylic esters by sodium ethoxide and its bearing on Claisen's condensation. J. KENYON and D. P. YOUNG (J.C.S., 1940, 216—218).—(+)- $\text{CHMeEt}\cdot\text{CO}_2\text{Et}$, b.p. $35^\circ/16$ mm., $\alpha_{\text{D}}^{20} +1.92^\circ$ (*l*, 0.5), and (—)- $\text{CHEtBu}\cdot\text{CO}_2\text{Et}$, b.p. $90\text{--}91^\circ/25$ mm., $\alpha_{\text{D}}^{20} -2.92^\circ$ (*l*, 2) (*dl*-acid partly resolved by cinchonidine), are readily racemised by conc. $\text{EtOH}\text{--NaOEt}$ (1 mol.), as is (—)- $\text{CHPhMe}\cdot\text{CO}_2\text{Me}$, b.p. $109\text{--}110^\circ/20$ mm., $\alpha_{\text{D}}^{20} -20.34^\circ$ (*l*, 0.5), by $\text{MeOH}\text{--KOME}$, indicating that formation of a sodio-derivative occurs in appreciable quantity and involves release of a proton from the α -C. Mechanisms postulating initial formation of $\text{Na}[\text{CHR}\cdot\text{CO}_2\text{Et}]$ (or modifications thereof) in Claisen's condensation are thus supported. H. B.

Isomeride of ricinoleic acid in fatty oil from seeds of *Vernonia anthelmintica*.—See A., 1940, III, 273.

Traumatic (Δ^a -decene- $\alpha\omega$ -dicarboxylic) acid.—See A., 1940, III, 271.

Deuterium compounds. Optically active sodium ammonium dideuterotartrate. H. ERLNMEYER and O. BITTERLIN (Helv. Chim. Acta, 1940, 23, 207—209).—Crystallisation of $\text{CO}_2\text{Na}\cdot\text{CD}(\text{OH})\cdot\text{CD}(\text{OH})\cdot\text{CO}_2\text{NH}_4$, $+4\text{H}_2\text{O}$, from H_2O at $<27^\circ$ gives the *d*-salt, $[\alpha]_{\text{D}}^{20}$ (anhyd.) $+31.48^\circ$ to $+31.69^\circ\pm 3^\circ$ in H_2O , which shows a definite effect of D on $[\alpha]$. R. S. C.

Determination of ascorbic acid.—See A., 1940, III, 236.

Constitution of arabic acid. III. Isolation of methyl heptamethylaldobionate from methylated degraded arabic acid. IV. Formation of 3-galactosidogalactose by hydrolysis of degraded arabic acid. J. JACKSON and F. SMITH (J.C.S., 1940, 74—78, 79—82).—III. Hydrolysis of the methylated Ba salt of degraded arabic acid (cf. A., 1940, II, 5) with $14\text{N}\cdot\text{H}_2\text{SO}_4$ yields a hexamethylaldobionic acid, which with 1% HCl in MeOH yields the α -form of the *Me* ester of hexamethyl-6- β -glucuronosidomethylgalactoside, and this when boiled with HCl in MeOH gives 2:3:4-trimethylmethylgalactoside and -glucuronoside, indicating that each side-chain in (I) consists of a terminal glucuronic acid group which is linked through at least one galactose (II) residue with the main (II) chain.

IV. A tentative structure proposed for (I) consists of twelve pyranose units (one terminal) and three terminal glucuronic acid residues. Both 1:3- and 1:6-glycosidic unions are involved, the presence of the former being shown by prolonged autohydrolysis of (I), which gives 3-galactosidogalactose, isolated by methylation as its Me_8 derivative, which was hydrolysed to 2:3:4:6-tetramethyl- and 2:4:6-trimethylgalactose. F. R. G.

Decomposition of thionylacetic acid in acid aqueous solution.—See A., 1940, I, 167.

Action of nitrous acid on formaldehyde. H. M. HALLIDAY and T. H. READE (J.C.S., 1940, 142—143).—Contrary to Vanino *et al.* (A., 1913, ii, 241), CH_2O is practically unaffected by HNO_2 (method: *loc. cit.*); the gaseous products are NO (94%; formed by thermal decomp. of HNO_2) and N_2 (6%; origin obscure). H. B.

High-temperature photolysis of acetaldehyde.—See A., 1940, I, 170.

Preparation of aliphatic aldehydes by catalytic dehydrogenation of alcohols in the liquid phase in the presence of reduced nickel. A. HALASZ (Compt. rend., 1939, 209, 1000—1003; cf. A., 1939, II, 376).—Lauryl alcohol (I) with 5% of its wt. of reduced Ni at $250^\circ/2$ hr. gives lauraldehyde (II) (20%), unchanged (I) (59%), and decomp. products of (I). Heating for shorter periods increases (I) and decreases (II), whereas heating for a longer period diminishes (I) and (II), the diminution in (II) being \propto the duration of heating. Increase in temp. favours

both the formation of (II) and the decomp. of (I). Moderate decrease in pressure is without effect on the reaction. *n*-Saturated C_{11} , C_{12} , C_{14} , C_{16} , and C_{18} aldehydes are isolated as their *semicarbazones*, m.p. 101°, 102.5°, 106.5°, 107°, and 107°, respectively.

J. L. D.

Raman effect and problems of constitution.
XIV. Methyl vinyl ketone.—See A., 1940, I, 146.

Stable and labile semicarbazones from methyl *n*-amyl ketone. W. S. RAPSON and R. G. SHUTTLEWORTH (J.C.S., 1940, 99).—Prep. of Me *n*-amyl ketone semicarbazone in aq. EtOH gives a labile form (I), m.p. 96—97°, which changes when left in the dark or in EtOH to the stable form (II), m.p. 121—123°. Inoculation of the solutions of (I) with (II) did not aid in separation of (II). (II) could not be converted into (I) by ultra-violet light. COMeBu^a and COMe-C₆H₁₃-*n* do not give labile semicarbazones.

F. R. G.

Keto-alcohols. I. α -Hydroxyketones. W. H. LINNELL and I. ROUSHDI (Quart. J. Pharm., 1939, 13, 252—259).—A series of α -OH-ketones has been prepared for pharmacological examination as analogues of deoxycorticosterone. The following have been prepared by interaction of ZnRI with chloroacetoxyisobutyl chloride and hydrolysis of the isolated *cycloacetal* with HCl-AcOH: CH_2Cl *Pr*^a ketone (I), b.p. 58—59°/17 mm. (*semicarbazone*, m.p. 209—210°); CH_2Cl *Bu*^a ketone (II), b.p. 94—95°/50 mm. (*semicarbazone*, m.p. 230—231°); CH_2Cl *n*-amyl ketone (III), b.p. 118—120°/50 mm. (*semicarbazone*, m.p. 240—241°). After refluxing with KOAc-EtOH followed by BaCO₃-H₂O, (I), (II), and (III) yield respectively *n*-butyryl-, b.p. 45°/12 mm. [2 : 4-dinitrophenylosazone, m.p. 234—236° (decomp.)], *n*-valeryl-, b.p. 97—99°/40 mm. [2 : 4-dinitrophenylosazone, m.p. 223—225° (decomp.)], and *n*-hexoyl-carbinol, b.p. 95—98°/15 mm. [2 : 4-dinitrophenylosazone, m.p. 245—246° (decomp.)], all of which reduce Fehling's solution and NH₃-AgNO₃ in the cold. Hexahydrobenzoyl chloride with CH₂N₂ gave an oil which evolved N₂ with H₂SO₄ in dioxan yielding hexahydrobenzoyl-carbinol, b.p. 95°/4 mm. [2 : 4-dinitrophenylhydrazone, m.p. 180—181° (decomp.)].

F. H.

Action of sodium borate on glucose and xylose. M. MURGIER and M. E. DARMOIS (Atti X Congr. Internaz. Chim., 1938, II, 737—742).—Measurements of $[\alpha]$ of solutions of glucose (I) and xylose (II) containing NaBO₂ show that the compounds C₆H₁₂O₆·2NaBO₂ and C₅H₁₀O₅·NaBO₂ are formed. (I) is probably combined in the α -furan form whilst (II) combines in the ordinary α -form. HBO₂ does not form compounds with these sugars.

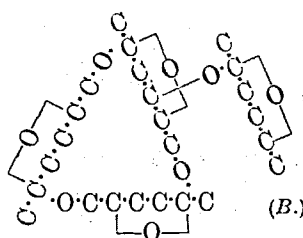
O. J. W.

Structure of γ -sugars. II. Stability of γ -fructose and heat of activation of its conversion into normal fructose. III. Preparation of 3 : 4 : 6-trimethylfructose. F. HARTLEY and W. H. LINNELL (Quart. J. Pharm., 1939, 12, 230—251, 743—752; cf. A., 1939, II, 142).—II. Polarimetric studies of the hydrolysis of sucrose by invertase at p_H 4.64, interrupting the hydrolysis, and completing the mutarotation of products with aq. NH₃ enable the rate of change of α of liberated fructose to be calc.

Postulation of a unimol. reaction for the conversion of γ -fructose (I) into equilibrium fructose by an acid-base catalysis mechanism based on the furanose formula for (I) is shown to be invalid. The mechanism of the conversion is shown to be (I) \rightarrow β -fructose (II) \rightarrow α + β -fructose. The half-life periods for (I) are 7.5 min. at 15° and 3 min at 25° and *E* for (I) \rightarrow (II) is 15,920 g.-cal. per g.

III. Trimethylfructose (III), obtained by hydrolysis of methylated inulin and purified through its methylfructoside and subsequent hydrolysis, gives an anhyd. phenylosazone, m.p. 134.5° (lit. 138°), identical with that of 3 : 4 : 6-trimethylglucose (IV). The hydrated phenylosazones of (III) and (IV) on recrystallisation from aq. EtOH have m.p. 88—89° and 85° (lit. 81—82°), respectively, each being raised to 134.5° after heating at 100°/2 mm. for 6 hr. An improved method of prep. of β -chloroglucosyl 3 : 4 : 6-triacetate 2-trichloroacetate is described. F. H.

Fructose anhydrides. XXII. Secalin. H. H. SCHLUBACH and C. BANDMANN (Annalen, 1939, 540, 285—297).—*Secalin* (I), *M* (in H₂O) 780—847, $[\alpha]_D$ -37.6° in H₂O, is isolated by the customary procedure from unripe rye stalks and purified by fractional pptn. from its conc. aq. solution with EtOH. Acetylation (Ac₂O in aq. 90% C₅H₅N at room temp.) gives the *acetate* (II) (44.8% Ac), $[\alpha]_D$ +3.0° in CHCl₃, hydrolysed (Zemplén) to (I), *M* 650—685, which thus differs from graminin (A., 1935, 69). Hydrolysis (N-H₂SO₄ at 20°; half-period 225 min.) of (I) affords fructose. Me₂SO₄-30% NaOH and (II) in COMe₂ and N₂ followed by MeI-Ag₂O give *methylsecalin* (46% OMe), $[\alpha]_D$ -45° in CHCl₃, which is converted by successive treatment with aq. EtOH-H₂C₂O₄, 0.25% HCl, and 0.25% MeOH-HCl into methylfructosides (A). Fractional distillation of the product from (A) and β -C₁₀H₇-COCl in C₅H₅N at 85° and then at 100°, affords tetramethylmethylfructoside, *trimethylmethyl-*



fructoside β -naphthoate, b.p. 145°/0.0001 mm., and *dimethylmethylfructoside* *di*- β -naphthoate (residue); suitable hydrolysis then gives 1 : 3 : 4 : 6-tetra-, (probably) 1 : 3 : 4-tri-, m.p. 75°, $[\alpha]_D$ (in MeOH) -8.3° \rightarrow -26.0° (in CHCl₃) +11.7° \rightarrow +18.7°, and a di-methylfructose, $[\alpha]_D$ (in MeOH) -14.6° \rightarrow -21.2°, -7.6° in CHCl₃ [probably identical with that obtained from sinistrin (A., 1936, 1096) and tritacin (A., 1937, II, 369)], respectively, in the ratio 1 : 2 : 1, thus showing that (I) has the constitution (B) (H and OH omitted). H. B.

Epimeric alcohols of the cyclohexane series. III. Glucoside formation. D. T. C. GILLESPIE, A. K. MACBETH, and J. A. MILLS (J.C.S., 1940, 243—245).—Contrary to Miescher *et al.* (A., 1938, II, 174), glucoside formation cannot be applied as a criterion of *trans*-configuration; both *cis*- and *trans*-forms of alcohols of the cyclohexane series react with aceto-bromoglucose (I). The following are obtained from the appropriate alcohol, (I), and dry Ag₂O in Et₂O :

l-menthyl-, m.p. 129.5°, $[\alpha]_D -90.3^\circ$, *d*-neomenthyl-, m.p. 144.5°, $[\alpha]_D +3.3^\circ$, *dl*-isomenthyl-, m.p. 103—105°, *dl*-neoisomenthyl-, m.p. 128—130°, *cis*-, m.p. 102°, $[\alpha]_D^{24} -32.8^\circ$, and *trans*-*dihydrocryptyl*-, m.p. 107.5°, $[\alpha]_D^{24} -25.8^\circ$, *cis*-, m.p. 105°, $[\alpha]_D^{24} -38.9^\circ$, and *trans*-1-3-methylcyclohexyl-, m.p. 103°, $[\alpha]_D^{24} -31.5^\circ$, *cis*-, m.p. 72—73°, $[\alpha]_D^{20} -23.4^\circ$, and *trans*-4-methylcyclohexylcarbonyl-, m.p. 113°, $[\alpha]_D^{20} -28.6^\circ$, *cis*-, m.p. 103—104°, $[\alpha]_D^{16} -25.8^\circ$, and *trans*-4-isopropylcyclohexylcarbonyl-, m.p. 112°, $[\alpha]_D^{16} -26.9^\circ$, and *cis*-(II), m.p. 106.5°, $[\alpha]_D^{20} -90.7^\circ$, and *trans*-1-cryptyl-, m.p. 99—99.5°, $[\alpha]_D -80.6^\circ$, -*d*-glucoside *tetra*-acetates. Ponndorf reduction of *l*-cryptone, reaction of the resulting *l*-cryptol with (I), and subsequent fractionation (aq. EtOH) gives (II). $[\alpha]$ are in EtOH.

H. B.

Polysaccharides. XXXIX. Constitution of levans formed by bacterial action. R. R. LYNE, S. PEAT, and M. STACEY (J.C.S., 1940, 237—241).—The polysaccharides produced (cf. Cooper *et al.*, A., 1935, 1419) from sucrose by *B. megaterium*, *Bact. pruni* (*Phytomonas pruni*), and *Bact. prunicola* (*P. prunicola*) are polyfructoses of the levan type; they are purified by repeated pptn. from aq. solution by MeOH and have $[\alpha]_D^{20} -40^\circ$, -45° , and -40° in H₂O, respectively. They are methylated (method: Challinor *et al.*, A., 1934, 760) to apparently identical methyl-levans (OMe 44.6, 44.8, and 44.5%, respectively), which give (method: *loc. cit.*) 1 : 3 : 4 : 6-tetramethyl- (10—12%) and 1 : 3 : 4-trimethyl-methylfructofuranoside, indicating that each levan consists of a chain of 10—12 contiguous fructofuranose units mutually linked through positions 2 and 6 (for structure, cf. *loc. cit.*); differences in physical properties are probably due to varying degrees of aggregation of the repeating unit. Anomalies in the $[\alpha]$ of levan acetates are due to incomplete acetylation (dependent on the amount of H₂O present in the reaction mixture); the more highly acetylated products show an increasing $+$ -rotation.

H. B.

Starch. K. FREUDENBERG, E. SCHAAF, G. DUMPERT, and T. PLOETZ (Naturwiss., 1939, 27, 850—853).—The space formulæ of α - and β -dextrin are discussed.

H. W.

Phosphorylation of the degradation products of starch. H. VOGEL (Ber., 1939, 72, [B], 2052—2053).—*iso*Trihexosan (I) is much less sol. in hot than in cold C₅H₅N. (I) which has separated from hot C₅H₅N contains no residue of glycerol and dissolves as freely in H₂O as (I). The individuality of (I) is thus confirmed. (I) is transformed by POCl₃ in C₅H₅N at -10° into the compound (II), C₆H₁₁O₈P, decomp. $\sim 150^\circ$, which contains 1 mol. of H₃PO₄ to each C₆H₁₀O₅ residue. It is almost insol. in cold H₂O, but swells in hot H₂O to a viscous jelly without passing into solution. It loses PO₄ completely when heated with the 8-fold amount of glycerol at 210°; the product (II) is hydrolysed by dil. H₂SO₄ to a product which strongly reduces Fehling's solution but does not give an osazone. Trihexosan gives a compound similar to (II). Isolable products are not afforded by tetra- or di- β -glucosan, β -glucosan, maltosan, lactosan, tetraglucosan, and more highly polymerised derivatives of glucosan.

H. W.

Formation and decomposition of glycogen-protein complex.—See A., 1940, III, 221.

Reduction of fatty acid amides under high pressure. I. S. UENO and S. TAKASE (J. Soc. Chem. Ind. Japan, 1939, 42, 409—410B).—Reduction of laur-, myrist-, and palmit-amide in dioxan containing CuO + Cr₂O₃ + BaO at temp. ranging from 240° to 310° and max. pressure 310 atm. proceeds: $R\cdot CO\cdot NH_2 + 3H = CH_2R\cdot NH_2 + H_2O$ and $2CH_2R\cdot NH_2 = NH_2 + (CH_2R)_2NH$. Since the second reaction is more rapid than the first the product is mainly *sec*. amine but contains a little primary amine. *Didodecylamine*, m.p. 51—53°, *ditetradecylamine*, m.p. 56—58°, and *dicetylamine*, m.p. 64—65°, are described.

H. W.

Cyclic structure of glucosaminides. A. NEUBERGER (J.C.S., 1940, 29—32).—The pyranoside structure of the α - and β -methylglycosides of glucosamine and its *N*-Ac derivative is proved by methylation of *N*-acetyl- α -methylglucosaminide with Me₂SO₄ and aq. NaOH, to its 3 : 4 : 6-Me₃ derivative, which was hydrolysed to 3 : 4 : 6-trimethylglucosamine hydrochloride (*N*-Bz derivative, m.p. 213°; $[\alpha]_D +124^\circ$ in moist C₅H₅N to $+105^\circ/48$ hr.), oxidised by 1-C₁₀H₇-SO₂-NHCl (2 equivs.) to 2 : 3 : 5-trimethyl-*d*-arabofuranose and by 3 equivs. to an imino-acid lactone, C₉H₁₅O₅N, m.p. 86.5°, $[\alpha]_D -40^\circ$ in CHCl₃.

F. R. G.

Nature of the carbohydrate residue in ovomucoid. I. **Glucosamine constituent.** M. STACEY and J. M. WOOLLEY (J.C.S., 1940, 184—191).—Ovomucoid (I) (prep. from coagulated egg-white by extraction with H₂O), $[\alpha]_D^{20} -57^\circ$ in H₂O, is freed from the polypeptide constituent by hydrolysis with boiling aq. 10% Ba(OH)₂ (containing some EtOH and a little C₅H₁₁·OH) in N₂ (cf. Fraenkel *et al.*, A., 1927, 862). The resulting carbohydrate residue (A), $[\alpha]_D^{21} \pm 0^\circ$ in H₂O, contains 5.5% total N (4.9 as NH₂-N) and is non-reducing; considerable deacetylation (cf. below) occurs during treatment with Ba(OH)₂. 5*N*-H₂SO₄ at 100°/70 hr. partly hydrolyses (A) and gives glucosamine, mannose, and a little galactose (identified as mucic acid) (cf. Hewitt, A., 1938, III, 949). Ac₂O-C₅H₅N at 70° (few min.) and then at 15°/24 hr. (vigorous shaking) converts (A) into a product (B) (O-Ac 29%), $[\alpha]_D^{25} -20^\circ$ in H₂O (in which it is readily sol.), hydrolysed [10% Ba(OH)₂ at 95°/1 hr.] to a *N*-Ac compound (Ac 11.5%), $[\alpha]_D \pm 0^\circ$ in H₂O. Attempts to methylate (I) and (A) with Me₂SO₄ + NaOH result in almost complete destruction of the polysaccharide but, under controlled conditions, (B) with Me₂SO₄-aq. NaOH-CCl₄, followed by Me₂SO₄-NaOH-COMe₂ and finally MeI-Ag₂O, gives a *N*-acetyl methyl derivative (II) (Ac 9.7, OMe 31.5%), $[\alpha]_D \pm 0^\circ$ in H₂O. Hydrolysis (2% MeOH-HCl for 48 hr.) of (II) affords 2-acetamido-3 : 4 : 6-trimethyl- α -methylglucoside (III), m.p. 149°, $[\alpha]_D^{20} +120^\circ$ in CHCl₃ ($\sim 10\%$), syrupy 3 : 4 : 6-trimethyl- α -methylglucosaminide [30%; acetylated (Ac₂O-MeOH) to (III)], partly methylated hexoses (C) (10%), and a syrup (D) ($\sim 50\%$). Thus, $<40\%$ of (II) is built up of methylated glucosamine residues; $<10\%$ of these are "end-groups" joined by glucosidic linkings to the rest of the mol. whilst $<30\%$ are joined through either the

NH₂-groups or, more probably, glucosidic linkings. Methylation (MeI-Ag₂O) of (C), subsequent hydrolysis (2N-H₂SO₄), and treatment with EtOH-NH₂Ph gives an approx. 4 : 1 mixture of tetramethyl-mannose- and -galactose-anilide. Methylation (MeI-Ag₂O) of (D) affords a light brown powder which appears to be a compound of AgI with glucosamine derivatives; a similar compound is obtainable from (III), MeI, and Ag₂O (cf. Irvine *et al.*, J.C.S., 1912, 101, 1128). Methylation [as for (B)] of (I) also affords (II), indicating that (I) contains NHAc-groups (cf. above) and that the 2-acetamidoglucose residues are end-groups joined by glucosidic linkings to the rest of the mol.

H. B.

Racemisation of amino-acids and depeptides on acetylation with keten. W. M. CAHILL and I. F. BURTON (J. Biol. Chem., 1940, 132, 161—169).—Acetylation of an NH₂-acid by keten in the presence of free alkali yields the optically active Ac derivative, but if free AcOH is allowed to develop racemisation occurs. When acetylated under such racemising conditions glycyl-*l*(—)-leucine yields a completely racemised derivative, whilst *l*(—)-leucylglycine yields a product with max. optical activity. This may be made the basis of a method for identifying terminal NH₂-acids in peptides.

F. G. M.

n-Nitrobenzoyl, m.p. 134°, and α -bromo-*m*-nitrobenzoyl, m.p. 125°, derivatives of deuterio- δ -aminovaleric acid. *dl*-Deutero-ornithine.—See A., 1940, III, 237.

Behaviour of some uramido-acids in the nitrous acid method for the determination of amino-nitrogen. A. G. GORNALL and A. HUNTER (Biochem. J., 1940, 34, 192—197).—The rate of liberation of N₂ and the vol. liberated after 2½ hr. at 25° in the reaction between 14 uramido-acids and HNO₂ (Van Slyke) is determined. ω -, α - with unbranched C chains, and α -uramido-acids with branched chains liberated 0.66—0.78, 1.25—1.42, and 1.98—2.00 atoms of N respectively with the exception of α -uramido-propionic (0.70) and -isohexoic acid (1.54 atoms of N).

A. L.

isoCarbamides and isoureides. V. Addition of dihydric and substituted alcohols to cyanamide. S. BASTERFIELD, F. B. S. RODMAN, and J. W. TOMECKO (Canad. J. Res., 1939, 17, B, 390—398; cf. A., 1930, 200).—Interaction of CN·NH₂ and HCl with CH₂·CH·CH₂·OH yields, as *hydrochloride* (an oil), *allylisocarbamide* (an oil) (*salicylate*, m.p. 126°; *benzoate*, m.p. 148°), which with CH₂Ac·CO₂Et (I) yields 2-*allyloxy*-4-*methyluracil*, m.p. 164°, and with CH₂(CO₂Me)₂ (II) gives *allylisocarbamide* 2-*allyloxybarbiturate*, m.p. 149—150°, which is hydrolysed (dil. HCl) to 2-*allyloxybarbituric acid*, m.p. 171°. Similarly are obtained *cyclohexylisocarbamide*, m.p. 77—78° (*hydrochloride*, m.p. 168°; *salicylate*, m.p. 153°), 2-*cyclohexyloxy*-4-*methyluracil*, m.p. 110°, *cyclohexylisocarbamide* 2-*cyclohexyloxybarbiturate*, m.p. 190°, and 2-*cyclohexyloxybarbituric acid*, m.p. 240°. *Benzylisocarbamide* with (I) yields a substance, C₂₀H₂₀N₄O₂, m.p. 153°, hydrolysed by HCl to 2-*benzyloxy*-4-*methyluracil*, m.p. 160°. Interaction of *m*-NO₂·C₆H₄·CH₂·OH with HCl and CN·NH₂ in Cl·[CH₂]₂·OH yields, as *hydrochloride*, *m*-nitrobenzyl-

H** (A., II.)

isocarbamide (*salicylate*, m.p. 137°). *Phenylethylisocarbamide* (*salicylate*, m.p. 158°) with (I) gives 2-*phenylethoxy*-4-*methyluracil*, m.p. 178°. Interaction of (CH₂·OH)₂ and CN·NH₂ in Cl·[CH₂]₂·OH with HCl gives, as *hydrochloride*, β -*hydroxyethylisocarbamide*, m.p. 158—159° (*salicylate*, m.p. 141.5°; *benzoate*, m.p. 134°). From OEt·[CH₂]₂·OH is obtained β -*ethoxyethylisocarbamide* (an oil) (*salicylate*, m.p. 101—102°), converted into 2-(β -*ethoxyethoxy*)-4-*methyluracil*, m.p. 121°, β -*ethoxyethylisocarbamide* 2-(β -*ethoxyethoxy*)*barbiturate*, m.p. 158—159°, and 2-(β -*ethoxyethoxy*)*barbituric acid*, m.p. 138°. NH₂·[CH₂]₂·OH and CN·NH₂ in Cl·[CH₂]₂·OH with HCl yield, after several months at 40°, β -*aminoethylisocarbamide dihydrochloride*, an oil (*disalicylate*, m.p. 141.5°; *di-benzoate*, m.p. 123°). From OH·[CH₂]₂·OAc is obtained β -*acetoxyethylisocarbamide* (*salicylate*, m.p. 138°; *benzoate*, m.p. 129°), and from OH·CH₂·CO₂Et, *carboethoxymethylisocarbamide hydrochloride*, which with KOH in Et₂O gives *carboxymethylisocarbamide* (*salicylate*, m.p. 136°; *benzoate*, m.p. 124°). Resorcinol and CN·NH₂ interact slowly in Cl·[CH₂]₂·OH with HCl to yield *m*-*hydroxyphenylisocarbamide hydrochloride* (*salicylate*, m.p. 138.5°; *benzoate*, m.p. 128°). J. D. R.

Reactions of carbonyl cyanide.—See A., 1940, I, 171.

Reaction of atomic hydrogen with azomethane.—See A., 1940, I, 165.

Action of Grignard reagents on heavy-metal salts. III. Mixed Grignard reagents and silver bromide. L. JOSEPH and J. H. GARDNER (J. Org. Chem., 1940, 5, 61—67; cf. A., 1930, 76; 1938, II, 53).—Some unsymmetrical product is formed when AgBr is added to a solution of MgPhBr and Mg alkyl bromide except when alkyl is Bu^γ. If the alkyl radicals are placed in order of decreasing electronegativity according to Kharasch they are also in order of decreasing yield of alkylbenzenes with the exception of Me and Et, of which the position is doubtful, and of increasing yield of Ph₂ (with exception of Me and Bu^γ). A similar regularity is observed in the case of CH₂Ph·MgCl and the same series of Mg alkyl halides. The yields of alkali benzyl increase and those of Ph₂ decrease as the series is descended except in the case of Bu^γ. This is to be expected since the CH₂Ph radical is less electronegative than any of the alkyls except Bu^γ. There is no regularity in the yields of dialkyls. The course of the reaction is probably determined by the relative electronegativities of the radicals involved, even when these include Ph and alkyls, in spite of the great difference in the stability of the corresponding Ag compounds. The great influence on the reaction of the nature of the halogen of the Grignard reagent (unpublished work) indicates that the electronegativity of the radicals is not the only significant factor. It is, however, probable that the effect of the halogen atom is confined to the initial stage of the reaction, that is the formation of the org. Ag compounds, whereas the electronegativity of the radicals determines the relative stability of the org. Ag compounds. Since it is possible to obtain quite large yields of the products formed by the coupling of radicals derived from org. Ag compounds of such greatly differing stability as AgPh

and AgBu^* , it seems reasonable to believe that the decomp. of a relatively stable org. Ag compound is promoted by the presence of a less stable compound undergoing decomp. If this is so, the change probably involves an interaction of 2 mols. of org. Ag compound, either the same or different. This is in agreement with the demonstration that free radicals are not involved. H. W.

Effect of alkyl iodides on the decomposition of cyclohexane. L. I. BERENZ and A. V. FROST (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 883—885).—*cyclohexane* (I) vapour containing AlkI was passed at atm. pressure through a SiO_2 tube at 580—600° (duration of heating ~ 11 sec.). The effect of the added iodides on the decomp. of (I) followed the sequence $\text{MeI} > \text{Pr}^i\text{I} > \text{Pr}^t\text{I} > \text{EtI}$, unsaturated gases being evolved. I alone had a considerably smaller effect; Na introduced into the vapour catalysed the decomp. of (I), the effect in presence of MeI being additive. J. L. D.

Allenes. II. Preparation of α -cyclohexyl- $\Delta^{\beta\gamma}$ -pentadiene. F. ACREE, jun., and F. B. LA FORGE (J. Org. Chem., 1940, 5, 48—53).—The action of α -chlorocrotonaldehyde on Mg hexahydrobenzyl iodide (I) affords γ -chloro- β -hydroxy- α -cyclohexyl- $\Delta^{\beta\gamma}$ -pentene (II), b.p. 130—135°/9 mm., m.p. 39—40°, which does not give a cryst. phenylurethane. It is reduced (H-Pd-CaCO_3 in KOH-EtOH) to α -cyclohexyl-pentane- β -ol, b.p. 112—114°/9 mm. PCl_5 and (II) in cold light petroleum yield $\beta\gamma$ -dichloro- α -cyclohexyl- Δ^{γ} -pentene, b.p. 131—133°/9 mm., which is converted by Zn dust in boiling EtOH into α -cyclohexyl- $\Delta^{\beta\gamma}$ -pentadiene (III), b.p. 82—85°/12 mm., which is relatively stable and does not appear to react with freshly prepared maleic anhydride. Hydrogenation (PtO_2 in EtOH) of (III) affords *n*-amylcyclohexane, b.p. 200—205°/atm. pressure. Ozonisation of (III) in CCl_4 followed by decomp. of the ozonide by H_2O yields MeCHO (dimethone derivative, m.p. 138—140°), cyclohexylacetaldehyde (semicarbazone, m.p. 157—159°), and cyclohexylacetic acid (IV) (amide, m.p. 169°). Oxidation (KMnO_4 in COMe_2) of (III) gives AcOH and (IV). $\beta\beta\gamma$ -Trichlorobutanol is reduced by (I) to $\beta\beta\gamma$ -trichlorobutan- α -ol, b.p. 97—98°/18 mm., m.p. 58—59°. H. W.

Magneto-chemical investigation of organic substances. XVII. True carbon diradical with "para" placed "free valencies." E. MÜLLER and H. NEUHOF (Ber., 1939, 72, [B], 2063—2075).—3 : 5-Dichloro-4-iodobenzophenone, m.p. 156° (corr.), formed by successive action of HNO_2 and KI on the 4- NH_2 -compound, is converted by Cu powder at 280° into 2 : 6 : 2' : 6'-tetrachloro-4 : 4'-dibenzoyldiphenyl (I), m.p. 243° (corr.), which with a small excess of LiPh in C_6H_6 at room temp. yields 2 : 6 : 2' : 6'-tetrachloro-4 : 4'-di(hydroxybenzhydryl)diphenyl (II), m.p. 271° (corr.). The presence of 2 active H in (II) is established by use of MgMeI in diisooamyl ether, anisole being an unsuitable solvent for *tert.* carbinols. If excess of LiPh is used or the temp. is allowed to rise a compound, $\text{C}_{30}\text{H}_{36}\text{O}_2\text{Cl}_2$, results by a Wurtz-Fittig synthesis. (II) is not affected by HCl in Et_2O and does not react satisfactorily with AcCl in C_6H_6 but

is transformed by pure SOCl_2 in boiling C_6H_6 into 2 : 6 : 2' : 6'-tetrachloro-4 : 4'-di(chlorobenzhydryl)diphenyl, m.p. 256° (corr.), which is readily converted by Hg in C_6H_6 under N_2 at room temp. into 2 : 6 : 2' : 6'-tetrachloro-4 : 4'-bisbenzhydryldiphenyl (III), m.p. 178° (corr.). The radical nature of (III) is established by its paramagnetism, measurements showing that in 2.3% solution $\sim 17\%$ at room temp. and $\sim 28\%$ at 80° is present as diradical. The orange colour of solutions of (III) is changed by short contact with air into a pale yellow-green but returns and can be again discharged until (III) is completely transformed into the peroxide. The absorption spectrum of (II) is related to that of 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\text{Bz}$ in the same manner as that of dimesityl to mesitylene and of 2 : 4 : 6 : 2' : 4' : 6'-hexachlorodiphenyl to 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Cl}_3$, thus establishing atropisomerism and differing from the relationship of COPh_2 to $(\text{C}_6\text{H}_4\text{Bz})_2$. 3 : 5-Dichloro-4-iodotoluene, m.p. 54° (corr.), from the 4- NH_2 -compound, is transformed by Cu powder at 280° into 2 : 6 : 2' : 6'-tetrachloro-4 : 4'-dimethyldiphenyl, m.p. 167° (corr.), which is converted by oxidation (CrO_3 in boiling AcOH) followed by esterification (CH_2N_2) into Me_2 2 : 6 : 2' : 6'-tetrachlorodiphenyl-4 : 4'-dicarboxylate, m.p. 116° (corr.); this with LiPh affords (II). In chemical and physical behaviour (III) appears as a doubled CPh_3 . Each half of the mol. behaves as if the other half were not present. The union between the CPh_3 systems is closed to π electrons. The absence of co-planar position of the C_6H_6 nuclei in (III) makes impossible a coupling by an electron pair of the second type and therefore the diradical form is the stable system for such a substance with non-planar arrangement of atoms. The author's views of the state of union of C in normal quinonoid hydrocarbons and, in general, in a C:C linking are confirmed. Reaction does not take place through a "valency tautomeric" diradical form but the electromeric, diamagnetic limit arrangements
$$>\text{C}:\text{C}< \longleftrightarrow >\text{C}-\text{C}< \longleftrightarrow >\text{C}-\text{C}< \longleftrightarrow >\text{C}-\text{C}< (\uparrow\downarrow)$$
 represent the actual reaction formulæ. The hypotheses of "valency tautomerism" should be abandoned in favour of the conception of mesomerism in the case of the C:C linking and corresponding systems. H. W.

Reactions in which diarylmethyl radicals can be detected. W. T. NAUTA, P. J. WUIS, and D. MULDER (Chem. Weekblad, 1940, 37, 96—99).—The products of the action of O_2 on diarylmethyls are reviewed. Free radicals are not obtained when the aryl groups are unsubstituted. When both *ortho*-positions are substituted the diarylmethyl has similar properties to CPh_3 . Diarylethanes containing 2 *ortho* and a *para*-substituent are also dissociated in solution. S. C.

Rate of dissociation of penta-arylethanes. W. E. BACHMANN and G. OSBORN (J. Org. Chem., 1940, 5, 29—39; cf. A., 1936, 1497).—The rate of absorption of I is measured by adding a weighed sample of the penta-arylethane to a measured vol. of a solution of I in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$, PhBr , xylene, or 1- $\text{C}_{10}\text{H}_7\text{Br}$ ($\text{C}_2\text{H}_4\text{Br}_2$, PhOMe , and PhCN are unsuitable) containing EtOH and $\text{C}_5\text{H}_5\text{N}$; the products are the triphenylmethyl Et ether and the diphenylmethyl-

pyridinium halide. After a given interval at const. temp. between 70° and 100° the mixture is quickly cooled, treated with an excess of standard $\text{Na}_2\text{S}_2\text{O}_3$, and back-titrated with standard I. In agreement with the results obtained on O absorption (*loc. cit.*) the rate-controlling step is a reaction of the first order corresponding with the unimol. process of dissociation. The energy of activation is 27.1 kg.-cal., in good agreement with the val. 27.6 kg.-cal. by the O method. Determinations of the rate const. and half-life periods of compounds $\text{CPh}_3\cdot\text{CHPhR}$ show that 9-phenanthryl, 1- C_{10}H_7 , and 2-fluoryl groups are most effective in promoting a rapid dissociation, the *p*-diphenyl and *p*- $\text{C}_6\text{H}_4\cdot\text{OMo}$ groups have an intermediate effect, whilst the *p*- $\text{C}_6\text{H}_4\text{Me}$ and Ph groups are least effective. CPh_3Na and phenyl-2-fluorylmethyl chloride give $\alpha\alpha\beta$ -tetraphenyl- β -2-fluorylethane, m.p. 152—162° in air and 164—168° in N_2 to an orange-coloured liquid. It is cleaved by HI to CHPh_3 and 2-benzylfluorene. 9-Benzoylphenanthrene is reduced by $\text{Al}(\text{OPr}^i)_3$ and Pr^iOH to phenyl-9-phenanthrylcarbinol, m.p. 139—140°, which is converted by HCl in dry C_6H_6 containing anhyd. CaCl_2 into phenyl-9-phenanthrylmethyl chloride (I), m.p. 114—116°, and by AcBr into the corresponding bromide, m.p. 115—116°. CPh_3Na and (I) in C_6H_6 give $\alpha\alpha\beta$ -tetraphenyl- β -9-phenanthrylethane, m.p. 176—188° in air and 190—193° in N_2 to a orange-red liquid, the constitution of which is established by cleavage (HI) to CHPh_3 and 9-benzylphenanthrene.

H. W.

1 : 5-Dimethylnaphthalene in coal tar.—See B., 1940, 259.

Trimethylnaphthalenes in coal tar.—See B., 1940, 259.

Ionene. ARNO MÜLLER (J. pr. Chem., 1939, [ii], 154, 82).—The colour reaction with *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and 10% H_3PO_4 (A., 1939, II, 78) is given by β - but not by pure α -ionene, which are thus 1 : 1 : 6-trimethyl-1 : 2 : 3 : 4- and -1 : 2 : 3 : 9-tetrahydronaphthalene, respectively.

R. S. C.

Action of nitric acid on anthracene. I. Action of nitric acid on anthracene in organic solvents, particularly acetic acid. II. Influence of various addenda on the action of nitric acid on anthracene in acetic acid. III. Mechanism of occurrence of 2 : 7-dinitroanthraquinone. R. ODA (J. Soc. Chem. Ind. Japan, 1939, 42, 414—417B, 417—418B, 418—421B).—I. Fuming HNO_3 (*d* 1.45) is added at room temp. to finely-divided anthracene (I) suspended in AcOH (~94%), if necessary with addition of H_2O . (I) dissolves completely and the filtered solution is then boiled under reflux for $\frac{1}{2}$ —1 hr. (I) is thus completely oxidised and partly nitrated. The mixture of anthraquinone (II) and 2 : 7-dinitroanthraquinone (III) is filtered and analysed by reduction with Na_2S and separation into (II) and 2 : 7-diaminoanthraquinone (IV) by treatment with H_3PO_4 (*d* 1.7) at ~150°. The proportion of (III) greatly increases with increasing H_2O content of AcOH and attains 50% with the mixture $\text{H}_2\text{O} : \text{AcOH} :: 3 : 8$ vol., after which it remains const. In complete absence of H_2O ($\text{AcOH}-\text{Ac}_2\text{O}-\text{HNO}_3$) there is no formation of

(III). Treatment of (I) with boiling $\text{HNO}_3-\text{H}_2\text{O}$ scarcely produces (III) if only a little HNO_3 is used. With $\text{H}_2\text{O}-\text{HNO}_3$ (*d* 1.4) : : 5 : 1 (vol.), (III) is formed in considerable amount but is very non-uniform, probably by reason of the heterogeneous nature of the change. In AcOH there is no nitration at 50°, the product being pure (II). In the product formed at 70° (III) is present in small amount whilst at 70—80° both oxidation and nitration occur. Nitration in COMe_2 , even if much H_2O is present, gives only (II) but the yield is small and much COMe_2 is required for the dissolution of (I). A mixture of (II) and (III) is obtained in EtOH but the reduced product is brown in colour and cannot be satisfactorily analysed by H_3PO_4 . In C_6H_6 or PhNO_2 only (II) is formed but the yields are bad.

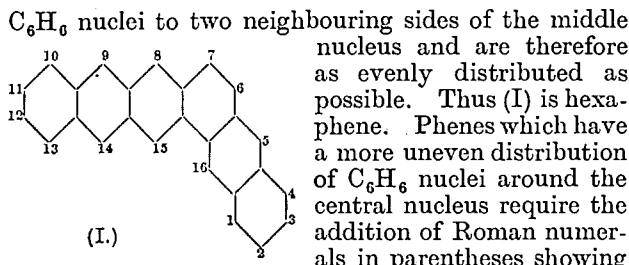
II. HNO_3 is without influence on the course of the reaction of HNO_3 on (I) in AcOH. In presence of H_2O_2 or other oxidising agent (aq. KMnO_4 , CrO_3) the product is exclusively (II). MeOH, EtOH, $(\text{CH}_2\cdot\text{OH})_2$, and glycerol have the same action as H_2O . $\text{Cu}(\text{NO}_3)_2$ can replace fuming HNO_3 for nitrating. It appears that HNO_3 has a definite nitrating action on the intermediate product from (I). An unsuccessful attempt is described to halogenate this product by the addition of Br to the filtrate from the action of HNO_3 on (I) in aq. AcOH at ~50°; the product is (II).

III. Nitration in AcOH alone proceeds in two directions whereas in aq. AcOH only nitroanthrone (V) is formed from which (II) is derived. The production of (III) in aq. AcOH must depend either on the peculiar behaviour of (V) or of HNO_3 in the binary mixture. (V) is in equilibrium with nitroanthranol (VI), which is the more reactive form. Since there is no evidence that the equilibrium $(\text{V}) \rightleftharpoons (\text{VI})$ is essentially different in aq. AcOH and AcOH it is more likely that the differences are due to variation in the behaviour of HNO_3 . In this connexion experiments with PhCHO , $\text{CH}_2\text{Ph}\cdot\text{OH}$, COPhBz , $\text{CHPh}_2\cdot\text{OH}$, and CH_2Ph_2 show that the oxidising power of HNO_3 in aq. AcOH is appreciably less than that in AcOH as is also the nitrating power. Thus benzanthrone is readily nitrated in AcOH but not in aq. AcOH. Since (VI) is a phenol it should be nitrated even in aq. AcOH. It is concluded that HNO_3 in aq. AcOH has a very slow oxidising and moderately powerful nitrating action on (VI) but that in AcOH it is very powerfully oxidising so that conversion into (II) is complete before nitration commences. 9-Bromo- and 9-methyl-anthracene are not nitrated.

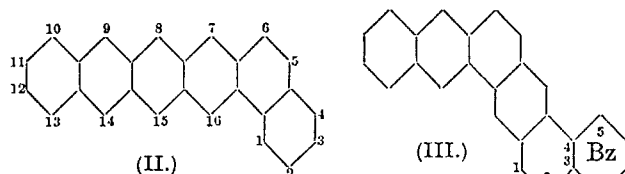
H. W.

Photopolymerisation of anthracene.—See A., 1940, I, 153.

Aromatic hydrocarbons. XXVI. Proposed nomenclature of condensed ring systems. E. CLAR (Ber., 1939, 72, [B], 2137—2139).—For hydrocarbons, like anthracene, formed by the linear compounding of C_6H_6 nuclei it is proposed to use the suffix -acene with a prefix indicating the no. of rings, e.g., triacene (anthracene), tetr-, pent-, hex-, hept-acene. Compounds related to phenanthrene receive the suffix -phene. This is used solely for hydrocarbons which are obtained by alternate addition of



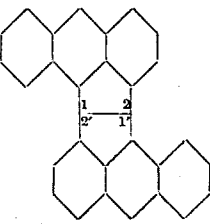
how many nuclei are on each side of the middle nucleus. Thus (II) is hexaphene (I—IV). According to this system a large no. of aromatic hydrocarbons



receive short names with use of a min. of figures; their derivatives are named in the usual manner. Thus (III) is 3:4-benzopentaphene. H. W.

Diphensuccindene series. XVIII. 9:12-Di-*p*-diphenyl- $\Delta^9:11$ -diphensuccindadiene. K. BRAND and H. W. STEPHAN (Ber., 1939, 72, [B], 2175—2180).— p - $C_6H_4Ph \cdot NO_2$ is reduced (NaSH) and the amine is converted through the diazo-derivative into p - C_6H_4PhI . The Grignard compound from this with diphensuccindane-9:12-dione gives 9:12-di-*p*-diphenylldiphensuccindane-9:12-diol, m.p. 249—250°, readily dehydrated by 90% HCO_2H in AcOH to 9:12-di-*p*-diphenyl- $\Delta^9:11$ -diphensuccindadiene (I), $C_6H_4Ph \cdot C \equiv C \cdot C_6H_4 \cdot o$ - $C_6H_4 \cdot C \equiv C \cdot C_6H_4Ph$, m.p. 367—368°, which when crystallised and in solution shows a similar colour to cryst. 9:12-diphenyl- $\Delta^9:11$ -diphensuccindadiene and its solutions. (I) is very slowly oxidised (CrO_3 in AcOH at room temp.) to 2:2'-di-*p*-phenylbenzoylbenzil, m.p. 235°, and 2-*p*-phenylbenzoylbenzoic acid, m.p. 230—231°. H. W.

Polynuclear hydrocarbons and their derivatives. XXV. Condensation products of anthrone with chloral. E. CLAR (Ber., 1939, 72, [B], 2134—2136).—Chloral (I) and anthrone in boiling AcOH give HCl, α,β -di-9:9'-anthroxylidene-ethane (II), m.p. 292°, and dihydrodianthrone (III). Reaction proceeds more rapidly in presence of $ZnCl_2$ but the ratio (II):(III) remains unchanged. The best results are obtained with $SnCl_2$ containing a trace of $Cu(OAc)_2$. The reducing action of $SnCl_2$ entirely suppresses the production of (III), and (II) is produced in good yield. If the condensation is effected in EtOH containing piperidine only (III) is produced, (I) acting as an oxidising agent. A similar result is obtained in conc. H_2SO_4 . Gradual addition of BzCl to (II)

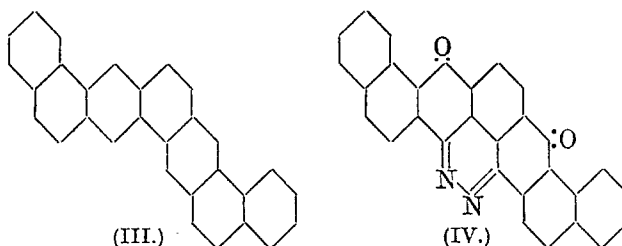


(V.)

in boiling $PhNO_2$ containing a trace of I leads to aceanthrono-2':1':1:2-aceanthrone (IV); $AcCl$, $CH_2Cl \cdot COCl$, or o - $C_6H_4(COCl)_2$ can replace BzCl and

$PhNO_2$ can be omitted if an acid chloride of high b.p. is used. Fusion of (IV) with $NaCl$, somewhat moist $ZnCl_2$, and Zn dust at 220° and subsequently at 280° gives aceanthreno-2':1':1:2-aceanthrene (V), m.p. 349° (decomp.). H. W.

Polynuclear hydrocarbons. XXVII. Benzo-*logues* of pentaphene and their derivatives. E. CLAR, F. JOHN, and R. AVENARIUS (Ber., 1939, 72, [B], 2139—2147).— p - $C_6H_4(COCl)_2$ 2- $C_{10}H_7Me$, and $AlCl_3$ in CS_2 give 1:4-di-2-methyl-1-naphthoylbenzene (I), m.p. 245—247°, whilst m - $C_6H_4(COCl)_2$ under similar conditions gives 1:3-di-2-methyl-1-naphthoylbenzene (II), m.p. 185°. When (I) or (II) is gently boiled until H_2O and oily matter cease to be evolved the products are the pale yellow 3:4-9:10- (III), m.p. 398—399°, and, probably the somewhat impure, red 1:2:8:9-, m.p. (indef.) 365—370°, -dibenzopentaphene. Oxid-



ation of (III) with CrO_3 in hot AcOH affords 3:4:9:10-dibenzopentaphene-5:14-8:13-diquinone, converted by $N_2H_4 \cdot H_2O$ in boiling C_5H_5N into 1:2-diaza-2:1-3:4-dinaphtho-1''-2''-9:10-pyrene-5:8-quinone (IV). It appears that the constitution of reaction products cannot be deduced when pyrolytic methods of formation are involved since ill-defined isomerisations frequently occur. The pyrolysis of (I) and (II) probably marks the limit of applicability of the method in its present form. As the no. of rings in the initial material increases the formation of fission products becomes more pronounced and the yields of complex substances are diminished. Under defined conditions p - $C_6H_4(COCl)_2$, 2- $C_{10}H_7Me$, and $AlCl_3$ in CS_2 yield p -2-methyl-1-naphthoylbenzoic acid, m.p. 196°. The similarly prepared p -2:4-dimethylbenzoylbenzoic acid, m.p. 187°, is converted by $SOCl_2$ followed by 2- $C_{10}H_7Me$ and $AlCl_3$ in CS_2 into 1-2':4'-dimethylbenzoyl-4-2''-methyl-1''-naphthoylbenzene, b.p. 350°/20 mm., m.p. 113-5°, which is pyrolysed to 11-methyl-3:4-benzopentaphene (V), m.p. 315—316°, and 2-methylanthracene. (V) is oxidised to the corresponding diquinone, which with $N_2H_4 \cdot H_2O$ in boiling C_5H_5N yields 1:2-diaza-5'-methyl-1':2':3:4-benzopentaphene-1''-2''-9:10-naphthopyrene-5:8-quinone. H. W.

Syntheses of substances with spasmolytic action. II. F. KÜLZ and K. W. ROSENMUND [with E. KAYSER, O. SCHWARZHAUPT, and H. SOMMER] (Ber., 1939, 72, [B], 2161—2167; cf. A., 1939, II, 107).—The spasmolytic action of $(CH_2Ph \cdot CH_2)_2NH$ (I) is increased by alkylation of the C_6H_6 nucleus; N -alkylation causes first a diminution but subsequently an increase in physiological action with increasing magnitude of the alkyl group, and also improves the solubility of the product without introducing undesired reactions. Lengthening of the

side-chains causes increase in activity in comparison with (I), which is very greatly enhanced by *N*-ethylation. Max. activity appears to be reached in $(\text{Ph} \cdot [\text{CH}_2]_3)_2\text{N} \cdot \text{Et}$. Hydrogenation of $p\text{-C}_6\text{H}_4\text{Me} \cdot [\text{CH}_2]_2 \cdot \text{NH}_2$ (II) and $\text{CH}_2\text{Ph} \cdot \text{CHO}$ in EtOH affords β -phenylethyl- β' -*p*-tolylethylamine (*hydrochloride*, m.p. 258°). (II) is converted by Pd-BaSO₄ in H₂ at 180–190° into di- β -*p*-tolylethylamine (*hydrochloride*, 270°). $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{Cl}$ and the requisite *sec.*-phenylethylalkylamines give the hydrochlorides, m.p. 160°, 137.5°, 154°, 142°, 82°, and 68°, respectively, of di(phenylethyl)-methyl-, -ethyl-, -propyl-, -butyl-, -*n*-amyl-, and -*n*-hexylamine. Catalytic reduction of the product from $\text{Ph} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$ and $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{CHO}$ gives di- γ -phenylpropylamine, b.p. 215°/12 mm. (*hydrochloride*, m.p. 200–201°). $\text{Ph} \cdot [\text{CH}_2]_3 \cdot \text{Cl}$, KOH, and NH_2Et in H₂O at 120° yield γ -phenylpropylethylamine, b.p. 115–118°/14 mm. (*hydrochloride*, m.p. 152°), and di- γ -phenylpropylethylamine, b.p. 165–168°/0.3 mm. (non-cryst. *hydrochloride*; perchlorate, m.p. 70°; reineckate, m.p. 155–156°). $\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{NH}_2$, b.p. 111–112°/12 mm., by Hofmann degradation of $\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{CO} \cdot \text{NH}_2$, and $\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{Cl}$ with anhyd. Na₂CO₃ in EtOH at 120° give di- δ -phenylbutylamine, b.p. 221–224°/6 mm. (*hydrochloride*, m.p. 179°). δ -Phenylbutylethylamine, b.p. 129–131°/15 mm. (*hydrochloride*, m.p. 147°), and di- δ -phenylbutylamine, b.p. 215–216°/3.5 mm. (non-cryst. *hydrochloride*; perchlorate, m.p. 88°), are described. Di- β -*p*-anisylethylamine, HCO₂H, and CH₂O at 120–130° give di- β -*p*-anisylethylmethylamine (*hydrochloride*, m.p. 194°). γ -Phenylpropyl- β :4-dimethoxyphenylisopropylethylamine, b.p. 195–198°/0.6 mm., gives a *hydrochloride*, m.p. 127–128° (m.p. appears variable). Catalytic reduction of a mol. mixture of CH₂Ph·NH₂ and $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{CHO}$ gives benzyl- γ -phenylpropylamine (*hydrochloride*, m.p. 187–188°). Benzyl- γ -phenylpropylethylamine has b.p. 183°/11 mm. Catalytic reduction of $\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{NH}_2$ and PhCHO in EtOH yields benzyl- δ -phenylbutylamine (*hydrochloride*, m.p. 196°); the *N*-Et derivative has b.p. 168°/0.6 mm. (*hydrochloride*, m.p. 117°). $\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{NH}_2$ and $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{Cl}$ yield β -phenylethyl- δ -phenylbutylamine, b.p. 198°/1.8 mm. (*hydrochloride*, m.p. 193°; *N*-Et derivative, b.p. 177°/1 mm., and its non-cryst. *hydrochloride*). γ -Phenylpropyl- δ -phenylbutylamine, b.p. 193°/0.5 mm. (*hydrochloride*, m.p. 180°), gives the *N*-Et derivative, b.p. 195–196°/2.5 mm. (*perchlorate*, m.p. 76°). β -*p*-Anisylethyl- γ -phenylpropylamine, b.p. 215–217°/3.2 mm. (*hydrochloride*, m.p. 257°), and β -*p*-anisylethyl- γ -phenylpropylethylamine, b.p. 205–207°/2 mm. (*perchlorate*, m.p. 96°), are described.

H. W.

Hydration of stearanilide. B. A. TOMS (*Nature*, 1940, 145, 227).—An EtOH solution of stearanilide (I), m.p. 93°, with a large excess of cold H₂O gives a gelatinous ppt. which becomes granular on keeping. Drying in a vac. over fused CaCl₂ for 10 days yields a white powder (A), decomp. 88–89°. (A) loses 79.1–79.8 wt.-% when dried to const. wt. at 55–90° for 3.5–14 hr.; the residue melts at 93°.

L. S. T.

Action of nitrous acid on *p*-nitrodimethylaniline in hydrochloric acid. H. M. HALLIDAY

and T. H. READE (*J.C.S.*, 1940, 138–141).—The reactions involved when a Me of $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ (I) is replaced by NO during treatment with NaNO₂ in 5*N*-HCl and N₂ at 17° are: $2p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{HCl}$ (II) + 3HNO₂ → $2p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe} \cdot \text{HCl}$ (III) + 2CH₂O + 3NO + H₂O + (H; not liberated; probably converts some NO into N₂); (III) + HNO₂ → $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO}$ (IV) + HCl + H₂O; CH₂O + 2HNO₂ → 2NO + CO₂ (little) and H₂O-sol. org. substances (m.p. 55° and 95–100°). The highest yield of (IV) is obtained with 5.5 mols. of NaNO₂ to 1 mol. of (I). Max. yield of CH₂O is by use of 2 mols. of NaNO₂; larger amounts of NaNO₂ give rapidly decreasing amounts of CH₂O. 1 mol. of CH₂O is decomposed by 2.2 mols. of NaNO₂ in 5*N*-HCl and N₂ at 15° to NO (+ a little N₂). It is probable that the HCl performs some function other than liberation of HNO₂ from NaNO₂.

A. T. P.

Additive reactions of unilaterally positivised systems. R. WIZINGER (*J. pr. Chem.*, 1939, [ii], 154, 1–39).—Examination of the behaviour of cyclic and acyclic ethylenes, derivatives of C₆H₆, aldehydes, ketones, carboxylic esters, lactones, acid amides, pyrone, coumarins, pyridones, quinolones, the corresponding CS-derivatives and imides, azo-compounds, and many others shows that every unsaturated system is able to form non-ionoid-ionoid additive products if the one atom of the unsaturated group is sufficiently positivised. The stability of the additive products increases with increase of the positive nature. If the latter is very strongly marked, the systems have the character of ansolvo bases and can even add metallic salts with the formation of complex compounds. If the non-ionoid adding atom is attached to H and the positivisation is only moderately marked, the non-ionoid-ionoid additive product undergoes spontaneous decomp. with elimination of acid and production of a substitution product. All such systems have therefore an aromatic character.

H. W.

Action of chlorine on arylthiocarbimides and reactions of arylisocyanodichlorides. G. M. DYSON and T. HARRINGTON (*J.C.S.*, 1940, 191–194).—PhNCS and Cl₂ in CHCl₃ (no cooling) give initially the dithiazole, $\text{NPh} \cdot \text{C}(\text{NPh}) \cdot \text{S}(\text{CCl}_2) \cdot \text{S}$ (I), which is hydrolysed (EtOH) to bis(phenylthiocarbimide) oxide, m.p. 118°, and converted by 1 Cl₂ into (probably) $\text{NPh} \cdot \text{C}(\text{SCl}) \cdot \text{NPh} \cdot \text{CCl}_2 \cdot \text{SCl}$ (II) and by 3 Cl₂ into $\text{NPh} \cdot \text{CCl}_2$ (cf. Helmers, A., 1887, 581). Similarly, RNCS (R = *m*- or *p*-tolyl; $p\text{-C}_6\text{H}_4\text{Br}$) give *bis*-*mtolyl*, m.p. 128°, *p*-*tolyl*, m.p. 139°, and *p*-*bromophenyl*-thiocarbimide oxide, respectively; no oxide is obtained when R = *o*-tolyl, *o*-, *m*-, or $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4$. PhNCS and more Cl₂ in CHCl₃ give a product which with boiling 40% aq. NaOH gives 1-anilinobenzthiazole, m.p. 159° (picrate, m.p. 221°), also obtained from CS(NHPh)₂ and Br in boiling CHCl₃, reducing the product with SO₂, and finally treating with hot 2*N*-NaOH. PhNCS and Cl₂ in $\text{NPh} \cdot \text{CCl}_2$ (solvent) give $\text{NPh} \cdot \text{CCl}_2$, b.p. 209–211° (cf. Sell *et al.*, A., 1875, 269). Similarly prepared (in CS₂) are: *p*-*bromophenyl*-, b.p. 122–124°/15 mm., *p*-anisyl-, b.p. 155–160°/15 mm., *o*-, b.p. 125–130°/15 mm., *m*-, b.p. 130°/10 mm.,

and *p*-tolyl-, b.p. 121—124°/20 mm., and (in CHCl_3) *m*-, m.p. 68°, b.p. 165—170°/15 mm. and *p*-nitrophenyl-isocyanodichloride, m.p. 80°. The *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ derivative is not obtained similarly; the product decomposes explosively at 100°. $\text{NR}\cdot\text{CCl}_2$ ($\text{R} = \text{Ph}$; *o*-, *m*-, or *p*-tolyl; *p*- $\text{C}_6\text{H}_4\text{Br}$; *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$) and AcOH in C_6H_6 give $\text{CO}(\text{NHR})_2$ (isolated) + AcCl , and thence $\text{NHR}\cdot\text{Ac}$. PhNCO is not formed as intermediate (cf. Sell *et al.*, *loc. cit.*). *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CCl}_2$ gives an intermediate compound, m.p. 278°. $\text{NPh}\cdot\text{CCl}_2$ and $\text{NH}_2\text{Ph}\cdot\text{C}_6\text{H}_6$ give triphenylguanidine hydrochloride. Similarly prepared (m.p. of corresponding hydrochloride in parentheses) are: phenyldi-*o*-, m.p. 100° (205°), *m*-, m.p. 93° (206°), and *p*-tolyl-, m.p. 109° (222—223°), phenyl-, oil (257—262°), and *p*-tolyl-di-*p*-bromophenyl-, m.p. 178° (262—266°), diphenyl-*p*-tolyl-, m.p. 128° (230°), tri-*o*-, m.p. 129° (213—215°), *m*-, m.p. 107° (221°), and *p*-tolyl-, m.p. 125° (231°), *o*-, m.p. 87° (205—208°), and *m*-tolyl-di-*p*-tolyl-, m.p. 105° (218°), tri-*p*-bromophenyl-, m.p. 126° [270—276° (decomp.)], *p*-bromophenyldi-*p*-tolyl-, m.p. 123° (251°), *m*-nitrophenyldi-*m*-, m.p. 139° (218—225°), and *p*-tolyl-guanidine, m.p. 179° (201—205°).
A. T. P.

Octahydro-dinaphthylene and -naphthidine. G. D. PARKES and G. N. WALTON (J.C.S., 1940, 201—202).—Azonaphthalene and Zn dust in boiling $\text{EtOH}\cdot\text{KOH}$ (2 hr.), then added to cold aq. HCl (24 hr.), give dinaphthylene and naphthidine, converted by $\text{Na}\cdot\text{C}_5\text{H}_{11}\cdot\text{OH}$ into ar-octahydrodinaphthylene (I), m.p. 213° (could not be acetylated or benzoylated; bis- NN' -phenylcarbamyl derivative, m.p. 168°), and ar-octahydronaphthidine, m.p. 50° (Ac_2 derivative, m.p. 317°), respectively. A suspension of (I) (in a little EtOH added to H_2O) and $\text{Me}_2\text{SO}_4\cdot\text{K}_2\text{CO}_3$ at 100° (bath) give tetramethyl-ar-octahydrodinaphthylene (II), m.p. 154°. Prepared similarly is tetramethyldi-naphthylene (III), m.p. 212° (methylation must be in alkali medium), reduced by $\text{Na}\cdot\text{C}_5\text{H}_{11}\cdot\text{OH}$ to (II). Quaternary salts could not be obtained from (II) or (III) but tetramethylnaphthidine and MeI give hexamethylnaphthidineammonium di-iodide, m.p. 220° (decomp.).
A. T. P.

Chemotherapy of azobenzenesulphonchloroamide series. II. *m*- and *p*-Derivatives. S. STERN and A. TAUB (J. Amer. Pharm. Assoc., 1939, 28, 1032—1036).—*m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and PhNO in AcOH at 80—90°, followed by boiling 0.1*N*- NaOH , afford azobenzene-*m*-sulphonamide, m.p. 168—169°, converted by NaOCl in aq. 2% NaOH into *Na* azobenzene-*m*-sulphonchloroamide (+2 H_2O) (I). *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$ is reduced (Zn dust, aq. KOH , >90°) and the colourless solution (hydrazo-compound?) allowed to oxidise spontaneously to *K* azobenzene-3:3'-disulphonate; the method of Mahrenholtz *et al.* (A., 1880, 804) leads to *K* azoxybenzene-3:3'-disulphonate. Azobenzene-3:3'- and -4:4'-disulphonamide with NaOCl -aq. NaOH yield *Na*₂ azobenzene-3:3'- (II) and -4:4'-di(sulphonchloroamide) (III) (each +4 H_2O). (I), (II), (III), and *Na* azobenzene-*p*-sulphonchloroamide have bactericidal activity (against *S. aureus*) comparable with that of chloramine-*T*.
F. O. H.

Replacement of diazo-group by hydrogen. H. H. HODGSON and E. MARSDEN (J.C.S., 1940, 207—208).— NH_2R , diazotised in HCl or H_2SO_4 , is added to aq. 1:5- $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$ or 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$, and the stabilised diazonium salt is dried at 30—40° and decomposed by Zn dust (Cu is slower) in EtOH (COMe_2 gives lower yields) at room temp. The decomp. appears to be a simple exchange of H from one SO_3H . The method is general; excellent yields are obtained from NH_2Ph , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{R}\cdot\text{NH}_2$ ($\text{R} = \text{Me}$, OMe , NO_2), *m*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, benzidine, α - and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, and many $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ and nitroaminodiphenyls.
A. T. P.

Diphenyl series. V. Preparation of asymmetrical diaryl derivatives. H. H. HODGSON and E. MARSDEN (J.C.S., 1940, 208—211).— RN_2Cl ($\text{R} = \text{Ph}$, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\cdot\text{NO}_2$, 1- and 2- C_{10}H_7 , etc.) is converted by 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, 1:5- $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$, or ZnCl_2 into the stabilised diazonium salt, which is decomposed in PhNO_2 (generally best), C_6H_6 (good), PhMe (practically unsuccessful), or C_{10}H_8 (ineffective), with, best, NaOAc in Ac_2O or AcOH , or $\text{EtOH}\cdot\text{KOH}$, anhyd. Na_2CO_3 , K_2CO_3 , NaOH , or KOH , at 0—5° and finally at 80°. Details of yields of Ph_2 derivative are recorded. Na_2CO_3 is better than NaOH or KOH . In C_6H_6 , $\text{EtOH}\cdot\text{KOH}$ is better than NaOH or KOH . The generalisation of Grieve *et al.* (A., 1935, 78) that a group invariably enters an aromatic nucleus PhR in the *p*- and/or *o*-positions with respect to R is confirmed and extended to $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot$ groups. Reactions in molten 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ give poor yields of products containing azo-compounds. Some Cl-derivative is formed when using ZnCl_2 . 3:4'-Dinitrodiphenyl, m.p. 137°, and 1-nitro-4-phenylnaphthalene, m.p. 151°, are new.
A. T. P.

Diazoamino-compounds. F. DWYER and J. C. EARL (Chem. and Ind., 1940, 136).—A reply to Mangini (cf. A., 1940, II, 12); it is suggested that his diazoamino-salts are contaminated with derivatives of $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}_2\text{Ph}$.
E. W. W.

Steric effect of the nitro-group on the orientation of a third substituent in *m*-nitrophenol. D. R. MEHTA and P. R. AYYAR (J. Univ. Bombay, 1939, 8, Part 3, 176—183).—*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (I) with CH_2O yields the CH_2 ether, m.p. 77°, of (probably) 6-nitro-2-hydroxybenzyl alcohol, oxidised (CrO_3 , AcOH) to (probably) 6-nitrosalicylic acid (II), m.p. 166—167°. $\text{Hg}(\text{OAc})_2$ and (I) in boiling EtOH yield 2(or 4 or 6)-acetoxymercuri-3-nitrophenol, m.p. 207—208°, which with NaCl gives the ClHg -derivative, m.p. 179—181°, and this with Br in aq. KBr yields 3:2:4:6:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}_3\cdot\text{OH}$. It is concluded that OH is the primary directive group in (I). The Reimer-Tiemann reaction with (I) gives a little 6:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHO}$ oxidised to ? (II).
F. R. G.

Free radicals and radical stability. VII. Influence of the phenoxyl group on stability of ketylic derivatives. Preparation of carbon monoxide from carbonates. S. T. BOWDEN and T. JOHN (J.C.S., 1940, 213—216).—The reaction $\text{Ph}_2\text{CO}_3 + 2\text{Na} = 2\text{NaOPh} + \text{CO}$ gives (in xylene; stirring at 110°) ~80% yield of CO sufficiently dry

to demonstrate the catalytic effect of moisture on combustion. Absence of colour in the reaction, and the fact that Et_2CO_3 similarly gives CO and NaOEt , suggests simple scission of Ph_2CO_3 . If the reaction involves the ketyl mechanism, the ketyl system must either be colourless or be readily changed into a colourless intermediate which loses NaOPh . It is possible that the reaction gives $\text{ONa}\cdot\text{CNa}(\text{OPh})_2$ and thence NaOPh and CO directly. Formation of $\text{CPh}_3\cdot\text{ONa}$ from $\text{Et}_2\text{CO}_3\text{--PhCl--Na}$ (Morton *et al.*, A., 1932, 157) is explained on the ketyl mechanism basis.

A. T. P.

Esters of sulphurous, chlorosulphinic, and chlorosulphonic acids. II. W. GERRARD (J.C.S., 1940, 218—230; cf. A., 1939, II, 97).—Mechanisms of replacement of OH by Cl using SOCl_2 , SO_2Cl_2 , COCl_2 , PCl_3 , or POCl_3 , in absence or presence of *tert.* bases or their hydrochlorides, are examined. Decomp. of $\text{OPh}\cdot\text{SOCl}$ by a *tert.* base or its hydrochloride occurs by different mechanisms and differs fundamentally from that of aliphatic chlorosulphinates by the same reagents. SOCl_2 (0.5 mol.), PhOH (1 mol.), and $\text{C}_5\text{H}_5\text{N}$ or quinoline ($\text{C}_9\text{H}_7\text{N}$) (1 mol.) in Et_2O at -5° give Ph_2SO_3 and $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ or $\text{C}_9\text{H}_7\text{N}\cdot\text{HCl}$, respectively. Ph_2SO_3 and SOCl_2 (excess) give $\text{OPh}\cdot\text{SOCl}$ (10% yield) (cf. Carré *et al.*, A., 1933, 48), which, with HCO_2H at room temp., gives HCO_2Ph (84% yield) or with *l*-menthol- $\text{Et}_2\text{O}\text{--C}_5\text{H}_5\text{N}$ at -5° , gives $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ and *Ph menthyl sulphite*, b.p. $156\text{--}160^\circ/2\text{--}3\text{ mm.}$, $\alpha_D^{20} +10\text{--}61^\circ$ ($l = 1$). $\text{OPh}\cdot\text{SOCl}$ and $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$, with or without Et_2O , do not react at room temp., but at 122° react explosively to give a substance free from N or Cl. $\text{OPh}\cdot\text{SOCl}$ is decomposed vigorously at 98° or 108° respectively by $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ or $\text{C}_9\text{H}_7\text{N}\cdot\text{HCl}$; it reacts explosively with NPhMe_2 at 16° , but slowly with $\text{NPhMe}_2\cdot\text{HCl}$ at 50° . Bu^a chlorosulphinates (I) and $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$ at $0\text{--}10^\circ$ give Bu^aCl , SO_2 , and, after treatment with dil. H_2SO_4 or aq. NaHCO_3 , solutions containing butyl-pyridinium or -quinolinium ion [*n*-butylquinolinium platinichloride has m.p. $223\text{--}224^\circ$ (decomp.)], respectively. Et α -chlorosulphinoxypionate (II) and $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$ give $\text{CHMeCl}\cdot\text{CO}_2\text{Et}$ (III), SO_2 , and some pyridinium or α -carbethoxyethylquinolinium salt (platinichloride, m.p. $170\text{--}171^\circ$), respectively. (II) and $\text{C}_9\text{H}_7\text{N}\text{--Et}_2\text{O}$ react similarly. $\text{OEt}\cdot\text{SOCl}$ and $\text{C}_9\text{H}_7\text{N}\text{--Et}_2\text{O}$ at -10° give ethylquinolinium chlorosulphinate. $\text{OPr}^a\cdot\text{SOCl}$ gives (?) $\text{C}_9\text{H}_7\text{N}(\text{Pr}^a)\text{SO}_2\text{Cl}$ and quinolinium sulphite. Me or Bu^a give solids, and Bu^b or *n*-amyl chlorosulphinates afford oils. $\text{OAlk}\cdot\text{SOCl}$ and $\text{NPhMe}_2\text{--Et}_2\text{O}$ at $< \text{room temp.}$ give oils. (II) and NPhMe_2 , in presence or absence of Et_2O , give (III), α -carbethoxyethyl sulphite (IV), a purple solid, and a substance, m.p. $120\text{--}124^\circ$. (I) similarly gives SO_2 , Bu^aCl , and Bu^a_2SO_3 . (II) and $\text{C}_9\text{H}_7\text{N}\cdot\text{HCl}$ or $\text{NPhMe}_2\cdot\text{HCl}$ at 60° or 97° , respectively, give excellent yields of (III); SO_2 is steadily evolved, and there is quant. recovery of the hydrochloride; (I) reacts similarly. Et lactate (2 mols.) and $\text{C}_5\text{H}_5\text{N}$, $\text{C}_9\text{H}_7\text{N}$, or NPhMe_2 (2 mols.) with SOCl_2 (1 mol.) at -10° give the respective base hydrochloride (100%) and (IV) (90% yield) (cf. Ritchie, A., 1935, 1223). Similarly, Bu^aOH gives Bu^a_2SO_3 . (I) and *l*-menthol- $\text{C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ give a quant. yield of $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$, and *l*-menthyl Bu^a sulphite, b.p. $98\text{--}99^\circ/1\text{ mm.}$ (II) and

Bu^aOH similarly afford α -carbethoxyethyl Bu^a sulphite, b.p. $141\text{--}142^\circ/19\text{ mm.}$ β -Octanol (1 mol.), SOCl_2 (0.5 mol.), $\text{C}_5\text{H}_5\text{N}$ (1 mol.), and Et_2O , even at -10° , give $\sim 100\%$ yield of $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ and β -octyl sulphite. β -Octanol and $\text{SOCl}_2\text{--Et}_2\text{O}$ (CO_2) give β -octyl chlorosulphinate (cf. Kenyon *et al.*, A., 1930, 598). Et mandelate (V), SOCl_2 , and $\text{C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ at -10° give $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ and, after further treatment with $\text{C}_5\text{H}_5\text{N}$, a solution affording α -carbethoxybenzylpyridinium ferrocyanide and $\text{CHPhCl}\cdot\text{CO}_2\text{Et}$ (VI). (V) and excess of SOCl_2 in Et_2O (CO_2) at -10° to 16° give α -carbethoxybenzyl chlorosulphinate, whence (VI). $\text{CHPhMe}\cdot\text{OH}$ and $\text{SOCl}_2\text{--Et}_2\text{O}$ at 16° give α -phenylethyl chlorosulphinate, which with $\text{C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ at -10° gives SO_2 , HCl , and CHPhMeCl (VII). $\text{CHPhMe}\cdot\text{OH}$ and $\text{SOCl}_2\text{--C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ at -10° afford (VII) and $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$. Pr^bOH and SOCl_2 (CO_2) at -5° , then at room temp., give $\text{OPr}^b\cdot\text{SOCl}$ (VIII), b.p. $55^\circ/40\text{ mm.}$, which with HCO_2H at room temp., then at 70° , gives SO_2 , HCl , and HCO_2Pr^b , or with $\text{C}_5\text{H}_5\text{N}$ at -10° gives SO_2 and Pr^bCl . (VIII) and $\text{C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ give an oil which affords isopropylpyridinium ferrocyanide. *sec*-Bu chlorosulphinate, b.p. $55\text{--}60^\circ/30\text{--}35\text{ mm.}$, and $\text{C}_5\text{H}_5\text{N}\text{--Et}_2\text{O}$ give an oil which affords *sec*-butylpyridinium ferrocyanide. Et lactate and SO_2Cl_2 or (IV) and dry Cl_2 give Et α -chlorosulphinoxypionate, b.p. $90\text{--}92^\circ/2\text{ mm.}$, converted by $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$ in Et_2O at -10° into (III) and $\text{C}_5\text{H}_5\text{N}\cdot\text{SO}_2$ or quinoline-sulphur trioxide, respectively. Ph chlorosulphonate does not react with $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_9\text{H}_7\text{N}$, with or without Bu^aOH , in the cold; NPhMe_2 reacts to give an oil. Et lactate (1 mol.) and COCl_2 (0.5 mol.) in $\text{PhMe}\text{--C}_5\text{H}_5\text{N}$ (1 mol.) at -10° give immediately $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ and α -carbethoxyethyl carbonate, b.p. $110\text{--}110.5^\circ/1\text{ mm.}$ (90% yield) (cf. Ritchie, *loc. cit.*). The action of COCl_2 on a OH-compound in presence of $\text{C}_5\text{H}_5\text{N}$ is analogous to that of SOCl_2 . PCl_3 (0.33 mol.), $\text{C}_5\text{H}_5\text{N}$ (1 mol.), and Bu^aOH , β -octanol, or (V) (1 mol.) in Et_2O give almost quant. yields of $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ (slower ptn. using POCl_3). A general theory to account for results of other workers is submitted. A. T. P.

Condensation of α -substituted acetoacetates with phenols. II. Use of various condensing agents with ethyl α -acetoglutarate. N. M. SHAH (J. Univ. Bombay, 1939, 8, Part 3, 205—207; cf. A., 1938, II, 502).—There is no especial influence of different condensing agents on the reaction between *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ (I) or 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$ with Et α -acetoglutarate (II), except that AlCl_3 is notably efficient for (I). Condensation does not occur with (II) and 1 : 2 : 3- $\text{C}_6\text{H}_3(\text{OH})_3$ (P_2O_5), α - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ (H_3PO_4), β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ (P_2O_5 or AlCl_3), or *m*- and *p*-cresol (all agents). F. R. G.

Bromine ion as brominating agent.—See A., 1940, I, 166.

New adrenal base. J. J. PFIFFNER and H. B. NORTH (J. Biol. Chem., 1940, 132, 461—462).—Adrenodiamine, a phenolic base, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$, m.p. $219\text{--}221^\circ$ (decomp.) [*dihydrochloride*, m.p. $215\text{--}216^\circ$ (decomp.; sinters $\sim 195^\circ$)], has been isolated from ox adrenals. It couples with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$, shows absorption max. at 231, 271, and 300 μ , and yields an O- Ac derivative, m.p. $176\text{--}177^\circ$ (decomp.), and a

Me₂ ether, m.p. 132—133° (decomp.). It has no pressor or oxytocic activity. M.p. are uncorr. (Berl block). P. G. M.

Synthesis of 4-hydroxymethyl-2- α -hydroxyethylanisole and its derivatives. M. ANGLADE (Compt. rend., 1940, 210, 52—54).—Saturation of a mixture of *p*-OMe·C₆H₄·CH₂Cl (I) (cf. Quelet *et al.*, A., 1936, 1504), (MeCHO)₃, conc. HCl, and H₃PO₄ with dry HCl followed by treatment with H₂O and then MeOH-NaOMe gives *p*-methoxymethylanisole, b.p. 107—108°/15 mm., unchanged (I), and 4-methoxymethyl-2- α -methoxyethylanisole (II) (18%), b.p. 144—145°/15 mm. *p*-Ethoxyethylanisole, b.p. 119—120°/18 mm., and 4-ethoxymethyl-2- α -ethoxyethylanisole, b.p. 157—158°/18 mm., are prepared similarly. (II) with AcCl in dry light petroleum containing ZnCl₂ gives 4-chloromethyl-2- α -chloroethylanisole, converted by NaOAc and then hydrolysis (40% EtOH-KOH at 100°) into 4-hydroxymethyl-2- α -hydroxyethylanisole (26%), m.p. 126° (phenylcarbamate, m.p. 142—143°), which is converted by warm KMnO₄ into 4:1:3-OMe·C₆H₃(CO₂H)₂. J. L. D.

Formation of ketyls by action of potassium on benzpinacol. T. JOHN and S. T. BOWDEN (J.C.S., 1940, 251—252).—Benzpinacol (I) or an equimol. mixture of CHPh₂·OH and CPh₂ behave similarly with K in xylene (N₂). The blue ketyl is formed, and on raising the temp. H₂ is evolved; colour changes are similar in either case. Hydrolysis of the mixture yields CHPh₂·OH and CPh₂. Reaction with CPh₂ alone is slow. It is indicated that the H of OH in (I) is directly replaced by metal to form the K and K₂ derivative, and the latter is partly dissociated into the unimol. ketyl (cf. Bachmann, A., 1933, 505; Doescher *et al.*, A., 1934, 1158) and is then reduced to CHPh₂·OK. (I) reacts quickly in the cold with CPh₃·OH to form the ketyl system and CPh₃·OH. Formation of CPh₃·OH from (I), PhBr, and Na depends on the formation of ketyls. A. T. P.

Fission of digitonides. W. BERGMANN (J. Biol. Chem., 1940, 132, 471—472; cf. Schoenheimer *et al.*, A., 1933, 500).—The digitonide is dissolved in 10—20 parts of dry C₅H₅N, kept at 70—100° for 1 hr., and evaporated to dryness in a vac. The residue is extracted with dry Et₂O and the extracts are evaporated, leaving the sterol (yield >90%). Treatment of the Et₂O-insol. residue with 90% EtOH and a further C₅H₅N treatment of undissolved digitonide raises the yield of recovered sterol (*e.g.*, cholesterol) to 95—98%. P. G. M.

Constitution of cholesterol. XVII. Isomerisation of cholesterol by hydrochloric acid. R. DE FAZI and F. PIRRONE (Gazzetta, 1940, 70, 18—26).—Cholesterol (I) in Et₂O-EtOH (all anhyd.) with HCl gives a cholesterol hydrochloride (II), m.p. 126—127°, [α]_D²⁵ -19.31° to -19.75° in C₆H₆ (cf. A., 1933, 710), which is shown by microscopic examination at the m.p. to consist of mixed crystals of two isomerides. After many crystallisations from EtOH, (II) gives a product, m.p. 128—129°, [α]_D²⁵ +7.21° to +7.81°. Possible structures, and products obtainable by loss of HCl, are discussed. In EtOH with NaOAc, (II) gives (I), an ischolesterol (III), m.p. 141—143° (cf.

A., 1938, II, 321), allocholesterol of m.p. 131—132° (IV), and Windaus' allocholesterol, m.p. 116—117° [consisting of mixed crystals of (I) and (IV)]. (III) consists of mixed crystals of (I) and an epicholesterol (V), m.p. 141—141.5°, [α]_D²⁵ -33.33° (acetate, m.p. 99—101°; Br₂-derivative, m.p. 103—104°). With AgNO₃ in EtOH, or with KOH-EtOH, (II) gives (I); with boiling Ac₂O, the acetate of (I); with NH₃-EtOH, or with C₅H₅N, (II) gives (III). With AcCl in C₅H₅N, (II) gives the chlorocholestanyl acetate, m.p. 148—150°, obtained by Wieland from (I), AcCl, and AlCl₃ (cf. A., 1931, 1412). E. W. W.

Constituents of the adrenal cortex and related substances. XXXII. Three stereoisomeric allopregnane-3(β):17:20-triols. H. REICH, M. SUTTER, and T. REICHSTEIN (Helv. Chim. Acta, 1940, 23, 170—180; cf. A., 1939, II, 317).—alloPregnane-3(β):17(α)-diol monoacetate and POCl₃-C₅H₅N at 135° give 3(β)-acetoxy- Δ^{17} -allopregnene, m.p. 120—121.5° (hydrolysed to the alcohol, m.p. 136—137°), which with OsO₄ in Et₂O followed by aq. EtOH-NaOH and CH₂O gives a mixture, separated by acetylation, crystallisation, and chromatography into substance *J* and an isomeric allopregnane-3(β):17:20-triol, m.p. 212—214° after sintering at ~205°, [α]_D²⁵ -16.7±2° in abs. EtOH [diacetate, m.p. 135—136° (corr.)], [α]_D²⁵ -18.2±1° in COMe₂; oxidised by HIO₄ to *t*-androsterone], with small amounts of substance *O*, a triol, C₂₁H₃₆O₃, m.p. 240—241°, [α]_D²⁵ -28.5±2° in abs. EtOH [diacetate, m.p. 160—161° (corr.)], [α]_D²⁵ -60.9±2° in COMe₂; with HIO₄ gives an oil and with CrO₃ an acid, C₂₁H₃₂O₄, m.p. 195—197°, and a compound, C₂₁H₃₂O₂, m.p. 197—199° (acetate, m.p. 207—209°; CrO₃ gives a neutral substance, C₁₉H₂₈O₂, m.p. 231—233°, and a small amount of an acid, m.p. 237—243°). R. S. C.

Synthesis of $\beta\beta$ -di-*p*-anisylpropionic acid. V. A. VYAS and K. V. BOKIL (Rasāyanam, 1939, 1, 195—197).—Di-*p*-anisylmethyl chloride, m.p. 93—94°, and CHNa(CO₂Et)₂ in C₆H₆ give an ester, hydrolysed by KOH-EtOH to di-*p*-anisylmethylmalonic acid, m.p. 182—183°, converted at 190° into $\beta\beta$ -di-*p*-anisylpropionic acid, m.p. 141—142°. A. T. P.

Synthesis of β -methoxy- β -phenyl- α -methylpropionic acid. Y. F. CHU, C. C. LUENG, and W. Y. YU (J. Chem. Eng. China, 1938, 5, 79—81).—CHMeBz·CO₂H is reduced (H₂, PtO₂, EtOAc, 80—90°) to *Et* β -hydroxy-, m.p. 120—121°, b.p. 120—125°/6.5 mm. (acid, m.p. 116—118°), the Na derivative of which in EtOH with MeI gives two forms of *Et* β -methoxy- β -phenyl- α -methylpropionate, b.p. 104—106°/27 mm., and m.p. 122—123° (free acid, m.p. 121—123° and 120.5—122.5°, respectively). F. R. G.

New products from the condensation of anisole with acetonedicarboxylic acid. I. $\beta\beta$ -Di-*p*-anisylbutyric acid. V. A. VYAS and K. V. BOKIL (Rasāyanam, 1939, 1, 198—200).—CO(CH₂·CO₂H)₂, PhOMe, and H₂SO₄ (~80 vol.-%) at room temp. give $\beta\beta$ -di-*p*-anisylglutaric acid, an acid, m.p. 90—91°, and $\beta\beta$ -di-*p*-anisylbutyric acid (I), m.p. 166—167° (Br₂-derivative, m.p. 83°); (I) heated with CaO gives $\beta\beta$ -di-*p*-anisylethylene. CH₂Ac·CO₂Et or *p*-methoxy-

β -methylcinnamic acid, PhOMe, and 80% H_2SO_4 give (I). A. T. P.

β -Phenyl- β -9-anthranylpropionic acids and their derivatives. P. E. GAGNON and R. HUDON (Trans. Roy. Soc. Canada, 1939, [iii], 33, III, 37—46; cf. A., 1935, 212).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{C}(\text{CO}_2\text{Et})_2$ and anthrone (piperidine as catalyst) give $\text{Et}_2\beta$ - p -nitrophenyl- β -9-anthranylolethane- $\alpha\alpha$ -dicarboxylate, converted ($\text{AcOH-H}_2\text{SO}_4$) into β - p -nitrophenyl- β -9-anthranylpropionic acid (I) (Ca salt: amide, m.p. 225—227°; anilide, m.p. $\sim 110^\circ$; Me, m.p. 202—203°, and Et ester, m.p. 137—138°) [oxidised by KOH-KMnO_4 at 100° (bath) to $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and anthraquinone (II)], the chloride (III), m.p. 170—175°, of which with AlCl_3 in C_6H_6 gives α -benzoyl- β - p -nitrophenyl- β -9-anthranylolethane, m.p. 170—172° (oxime, m.p. 187—188°). α -Benzoyl- β - m -nitrophenyl- β -9-anthranylolethane, m.p. 174—176° (oxime, m.p. 189—190°) (cf. loc. cit.), is prepared similarly. With AlCl_3 in CS_2 , (III) gives, after pouring on to ice and steam-distilling the product, (I) and a trace of orange-yellow substance. With conc. H_2SO_4 , (I) gives no hydrindone or benzanthrone. β -Phenyl- β -9-anthranylpropionic acid (A., 1933, 949) is oxidised by KOH-KMnO_4 at room temp. to β -phenyl- β -9-hydroxy-9-anthranylpropionic acid [converted by heating, or by CaCl_2 in C_6H_6 , into the corresponding lactone, m.p. 213—215°, which is slowly oxidised (KOH-KMnO_4 at 100°) to (II) and BzOH]. E. W. W.

Arylation of oils and fats. III. Synthesis of tolylstearic acid, methyl tolylstearate, and tolylstearo- p -xenylamide. W. KIMURA and J. TSURUGI (J. Soc. Chem. Ind. Japan, 1939, 42, 390—391b).—Camellia oil with AlCl_3 and PhMe in CS_2 yields mixed tolylstearic acids, purified through the Me esters, from which a p -xenylamide, m.p. 86.5°, is isolable as the main product. J. D. R.

Condensation of ethyl acetoacetate with phenols and phenolic ethers. I. Synthesis of p -methoxy- and p -ethoxy- β -methylcinnamic acids. D. B. LIMAYE (Rasāyanam, 1939, 1, 186).— $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and PhOMe or PhOEt with H_2SO_4 give low yields of p -methoxy- or -ethoxy- β -methylcinnamic acid, respectively; an acid, $\text{C}_{13}\text{H}_{20}\text{O}_4$, m.p. 163—164°, is also obtained from PhOMe. A. T. P.

Nitrocinnamoyl derivatives. M. FRERI and A. SOLZA (R.C. Atti Accad. Lincei, 1939, [vi], 29, 691—695).—Et p -nitrocinnamate with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH gives β -hydrazino- β -nitrophenylpropionhydrazide, m.p. 147°, converted by conc. HCl into the hydrochloride (I), m.p. 196—198°, of p -nitrocinnamhydrazide; attempts to isolate the latter give only polymerides. With the appropriate aldehydes in EtOH-NaOH (until neutral), (I) gives anisaldehyde-, m.p. 174°, piperonal-, m.p. 217°, and vanillin- p -nitrocinnamoylhydrazones, m.p. 240°. With NaNO_2 in H_2O under Et_2O , (I) gives p -nitrocinnamazide, m.p. 123°. Di- o -, m.p. 301°, and - m -nitrocinnamoylhydrazine, m.p. 302°, are prepared from the appropriate acyl chlorides, in EtOH. E. W. W.

Tautomerism of phenylbutenoic acids. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1939, 8, Part 3, 184—189).—Deoxybenzoin (I),

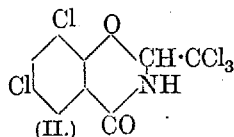
$\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn in C_6H_6 yield the Et ester (II), m.p. 60°, of β -hydroxy- β - γ -diphenylbutyric acid, m.p. 126—127°, which with Ac_2O gives β - γ -diphenyl- Δ^2 -butenoic acid (III), m.p. 114° [ozonolysis product, (I); anilide, m.p. 135°; p -toluidide, m.p. 156°; Ag salt; Et ester, b.p. 210°/10 mm.]. (II) in C_6H_6 with P_2O_5 yields the Et ester, b.p. 210—215°/12 mm., of β - γ -diphenyl- Δ^2 -butenoic acid (IV), m.p. 173° (Ag salt; anilide, m.p. 172°; p -toluidide, m.p. 160—161°). The equilibrium between (III) and (IV) by the Kon-Linstead-Wright bromometric method occurs at 17% of (III) with a mobility of 0.89. β -Hydroxy- α - β -diphenylbutyric acid, m.p. 192° (lit. 182°) (Ag salt; Et ester, b.p. 130°/10 mm.), with Ac_2O yields α - β -diphenyl- Δ^2 -butenoic acid, m.p. 160° (Ag salt; anilide, m.p. 148°), which could not be converted into the Δ^2 -isomeride and this could not be prepared in any other way. F. R. G.

Interaction of sulphuryl chloride with arylamides of aromatic acids. III. G. V. JADHAV and D. R. SUKHATANKAR (J. Univ. Bombay, 1939, 8, Part 3, 170—172; cf. A., 1939, II, 263).—Chlorination of m - and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{R}'$ with SO_2Cl_2 is effected under (usually) drastic conditions; the mol. is deactivated by the NO_2 . The following were prepared: m -nitrobenz- p' -chloroanilide, m.p. 175°, - o' -toluidide, m.p. 154°, -5'-chloro- o' -toluidide, m.p. 183°, and -3'-chloro- p' -toluidide, m.p. 173°; p -nitrobenz- p' -chloroanilide, m.p. 219°, -5'-chloro- o' -toluidide, m.p. 210°, and -3'-chloro- p' -toluidide, m.p. 158°. Constitutions are proved by hydrolysis or synthesis. F. R. G.

Dehydration product of chloral-3:5-dichlorosalicylamide. N. W. HIRWE and K. N. RANA (J. Univ. Bombay, 1939, 8, Part 3, 243—246).—Chloral-3:5-dichlorosalicylamide (I) dehydrated with conc. H_2SO_4 (or Ac_2O in aq. NaOH) yields 6:8-dichloro-2-trichloromethylbenzoxetazone (II), m.p. 176—177° (Ac derivative, m.p. 123—125°), which with conc. aq. NH_3 gives 3:5-dichlorosalicyl- $\beta\beta$ -trichloro- α -aminoethylamide m.p. 125—127° (Ac_2 derivative, m.p. 207—208°; hydrochloride; sulphate); this with HNO_2 yields (I).

F. R. G.

Characterisation of carboxylic acids as amides with the aid of carbodi-imides. VI. Characterisation of aromatic carboxylic acids as ureides [acyldiarylcarbamides]. F. ZETTSCHKE and G. RÖTTGER (Ber., 1939, 72, [B], 2095—2098).—The basic ureides of o -acids have the palest colours and are followed successively by those of the m - and p -acids. In relationship to the parent $\text{NBzAr}\cdot\text{CO}\cdot\text{NHAr}$ (I), o -substitution has invariably a distinct hypsochromic effect. The m -compounds resemble (I) whereas the colour of the p -compounds is often remarkably deepened. The pyridinecarboxylic acids, as examples of heterocyclic acids, fall exactly into line with the C_6H_5 series since the ring-N behaves as a substituent. Owing to the incompletely aromatic degree of saturation of the furan and thiophen ring systems, the 2-carboxylic acids differ considerably from pyridine-2-carboxylic



acid. The hypsochromic action of *o*-substitution is also obvious in poly-substitution. Carbodi-*p*-dimethylaminophenylimide with the following acids gives the appropriate *aroyldi-p-dimethylaminophenyl-carbamide*: *o*-, m.p. 151°, and *m*-, m.p. 137.5°, -toluic; *o*-, m.p. 158°, softens at 156°, and *m*-, m.p. 136°, -anisic; *o*-, m.p. 149°, softens at 148°, *m*-, m.p. 138°, softens at 135°, and *p*-, decomp. 215°, softens at 162°, -chlorobenzoic; *o*-, m.p. 153—155°, *m*-, m.p. 139—141°, and *p*-, decomp. 210°, softens at 168°, -bromobenzoic; *o*-, m.p. 158°, *m*-, m.p. 133°, and *p*-, m.p. 218—220°, -iodobenzoic; *o*-, m.p. 212—215°, *m*-, m.p. 144°, and *p*-, m.p. 226° after softening at 221°, -cyanobenzoic; pyridine-4-carboxylic, m.p. 195°, softens at 145°; 2-methylpyridine-3-carboxylic, m.p. 140°; veratric, m.p. 195°, softens at 141°; pentachlorobenzoic, decomp. 160°; pentachlorocinnamic, m.p. 215°, softens at 175°.

H. W.

Components of bark of *Rhamnus japonica*.

IV. Nucleus of α -sorigenin. Z. NIKUNI and H. HAYASHI (J. Agric. Chem. Soc. Japan, 1939, 15, 1179—1182; cf. A., 1939, II, 264).—Oxidation of dimethyl- α -sorigenin with alkaline KMnO_4 yields a trimethoxymaphthalene-2:3-dicarboxylic acid, m.p. 258—261° (anhydride, m.p. 263—264°), and distillation of diacetyl- α -sorigenin with Zn in H_2 yields 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$. α -Sorigenin must be a derivative of the lactone of 3-hydroxymethyl-2-naphthoic acid.

J. N. A.

Reactivity of the methylene group in β -arylglutaconic esters. I. D. B. LIMAYE and V. M. BHAVE (Rasāyanam, 1939, 1, 177—180; cf. A., 1931, 1055; 1934, 890).— Et_2 β -*p*-anisylglutaconate (I), b.p. 195—200°/5 mm., and EtOH -free NaOEt in Et_2O give the Na derivative, which with MeI affords Et_2 β -*p*-anisyl- α -methylglutaconate, whence the free acid, m.p. 145° (decomp.). Its anhydride, m.p. 108°, and Ac_2O - NaOAc at 100° (bath) give β -*p*-anisyl- α -methylglutaconylacetic acid, m.p. 125°. (I) and PhCHO in EtOH - NaOEt give β -*p*-anisyl- α -benzylideneglutaconic acid, m.p. 229° (*Et II*, m.p. 155°, and Et_2 ester, b.p. 225°/5 mm.; anhydride, m.p. 132°, gives no colour with FeCl_3). Et_2 β -6-methoxy-m-tolylglutaconate, b.p. 200—205°/5 mm., affords β -6-methoxy-*m*-tolyl- α -benzylideneglutaconic acid, m.p. 210° (*Et H* ester, m.p. 102°). β -4-Methoxy-*m*-tolyl- α -benzylideneglutaconic acid has m.p. 190° (cf. A., 1935, 343). $\text{Et}_2\text{C}_2\text{O}_4$ (I), and EtOH -free NaOEt in Et_2O give a substance, m.p. 125°.

A. T. P.

Condensation of acetonedicarboxylic acid with phenols and phenolic ethers. III. 4:6-Dimethoxy-*m*-phenylenebis- β -glutaconic acid. V. M. BHAVE and D. B. LIMAYE (Rasāyanam, 1939, 1, 180—182; cf. A., 1931, 1055; 1935, 343).— $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$, $\text{m-C}_6\text{H}_4(\text{OMe})_2$, and conc. H_2SO_4 at <5° give 4:6-dimethoxy-*m*-phenylenebis- β -glutaconic acid, m.p. 218° (decomp.), oxidised by aq. KMnO_4 - Na_2CO_3 to a mixture (A) of an acid, m.p. 220°, and 4:6:1:3- $(\text{OMe})_2\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2$, m.p. 266° (decomp.); the latter only is formed from (A) and H_2O_2 - AcOH . A. T. P.

Norcamphoric acid. H. GAULT and L. DALTROFF (Compt. rend., 1939, 209, 997—999; cf. A., 1938, II, 444).— Et cyclopentanone-2-carboxylate (I) with

CH_2O in presence of K_2CO_3 gives a mixture (A) of (I) with Et 2-hydroxymethylcyclopentanone-2-carboxylate, inseparable by distillation or extraction with alkali. Acetylation of (A) and distillation affords Et 2-acetoxy- Δ^1 -cyclopentene-1-carboxylate, b.p. 130°/17 mm., and Et 2-acetoxyethylcyclopentanone-2-carboxylate (II), b.p. 160°/17 mm. Hydrolysis (KOH) of (II) gives (by ring fission and recyclisation) cyclopentane-1:3-dicarboxylic (norcamphoric) acid, m.p. 121°.

J. L. D.

Synthesis of $\alpha\alpha$ -dimethyltricarballic and α -1-carboxycyclopentylsuccinic and α -1-carboxy-3-methylcyclopentylsuccinic acids. R. D. DESAI and G. S. SAHARIYA (J. Univ. Bombay, 1939, 8, Part 3, 235—238).—cyclopentanone cyanohydrin with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ in EtOH followed (after 48 hr. at room temp.) by $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (Chatterjee, A., 1937, II, 377) leads to 1-carboxycyclopentylsuccinic acid, new m.p. 165° (decomp.) (anil-anilide, m.p. 156°, and *p*-tolil-*p*-toluidide, m.p. 189—190°). Prepared similarly were Et_2 α -cyano- α -1-cyano-3-methylcyclopentylsuccinate, b.p. 205°/12 mm., hydrolysed to 1-carboxy-3-methylcyclopentylsuccinic acid, m.p. 144° (*p*-tolil-*p*-toluidide, m.p. 167° with previous sintering), and Et_2 $\beta\gamma$ -dicyano- γ -methylbutane- $\alpha\beta$ -dicarboxylate, b.p. 176—178°/5 mm., hydrolysed to $\alpha\alpha$ -dimethyltricarballic acid, new m.p. 160° (anil-anilide, m.p. 140°; *p*-tolil-*p*-toluidide, m.p. 170°).

F. R. G.

Methylation of ethyl methylcyclohexylidenecyanoacetates and reduction of ethyl 2-methylcyclohexylidenecyanoacetate. R. D. DESAI and G. S. SAHARIYA (J. Univ. Bombay, 1939, 8, Part 3, 239—242).—Methylation of the appropriate Et methylcyclohexylidenecyanoacetate with MeI in EtOH - NaOEt leads to Et α -cyano- α -4-, b.p. 152—154°/12 mm., Et α -cyano- α -3-, b.p. 146—147°/12 mm., and Et α -cyano- α -2-methyl- Δ^1 -cyclohexenylpropionate, b.p. 144—145°/12 mm., which with MeOH - NaOMe give respectively α -4-methyl-, b.p. 106°/12 mm., α -3-methyl-, b.p. 107—108°/12 mm., and α -2-methyl-cyclohexylidenepropionitrile, b.p. 110°/12 mm. The main product of the reduction of Et 2-methylcyclohexylidenecyanoacetate with Al-Hg in moist Et_2O is Et 2-methylcyclohexylcyanoacetate, b.p. 135—136°/12 mm., hydrolysed (KOH in EtOH) to 2-methylcyclohexylmalonic acid, m.p. 154°.

F. R. G.

Manufacture of aromatic dinitriles.—See B., 1940, 191.

Constitution of bile acids. G. GIACOMELLO (Gazzetta, 1939, 69, 790—801).—The complex, m.p. 186.5—188°, of deoxycholic (I) with palmitic acid was prepared by crystallisation of the 8:1 mol. mixture from EtOH ; the complex of (I) with cerotic acid was similarly prepared. Fourier analysis applied to the Patterson projection of X-ray reflexions from these complexes indicates the spatial configuration of (I) (cf. A., 1938, I, 440; 1939, II, 371). The bearing of the results on the constitution of bile acids in general is discussed.

F. O. H.

Acylation of aldoximes. III. Configuration of diphenylcarbamy and picryl ether derivatives

prepared from *syn*-aldoximes. G. VERMILLION, A. E. RAINSFORD, and C. R. HAUSER. IV. Benzoylation of *syn*- and *anti*-aldoximes. G. VERMILLION, E. JORDAN, and C. R. HAUSER (J. Org. Chem., 1940, 5, 68—74; 75—79).—III. The $\text{NPh}_2\cdot\text{CO}$ derivatives obtained by Brady *et al.* (A., 1926, 69) from the Na salts of *syn*-aldoximes (I) and $\text{NPh}_2\cdot\text{COCl}$ in CHCl_3 may also be obtained in warm KOH-EtOH ; formation of nitrile can be avoided by performing the reaction at a low temp. Under the same conditions *anti*-aldoximes (II) give nitrile directly. It is probable that (I) and $\text{NPh}_2\cdot\text{COCl}$ give the corresponding *syn*-derivatives, which are slowly transformed by warm alkali into nitrile, whereas (II) give the corresponding *anti*-derivatives, which are immediately decomposed. Inversion of configuration does not therefore take place during the action of $\text{NPh}_2\cdot\text{COCl}$ on (I). Reactions of a pair of geometrically isomeric acyl aldoximes differ only in degree, not in kind; whilst *anti*-isomerides probably always eliminate $\text{HO}_2\text{CR}'$ to form nitrile much more readily than the *syn*-isomerides, certain of the latter also, under certain conditions, may give mainly nitrile. Also in both cases hydrolysis to the corresponding oxime may occur. The $\text{NPh}_2\cdot\text{CO}$ derivatives are regarded as examples of acyl *syn*-aldoximes which undergo hydrolysis only with great difficulty; consequently, the elimination reaction predominates on heating with alkali. Attempts to hydrolyse these derivatives with hot or cold alkali or $\text{NH}_3\text{-EtOH}$ give only traces of aldoxime. The picryl ether derivatives of oximes appear very difficult to hydrolyse but that of *syn*-3 : 4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ (III) undergoes some hydrolysis in presence of alkali at room temp. or below, giving (III). Under the same conditions the isomeric *anti*-compound is recovered almost unchanged. Although the yield of (III) is low, its formation supports the view that the derivative has the *syn*-configuration. The $\text{C}_5\text{H}_5\text{N-NH}_2\text{Bu}^a$ test is not applicable to these compounds. *anti*-3 : 4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ and *anti*-*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ are relatively stable towards $\text{C}_5\text{H}_5\text{N-NH}_2\text{Bu}^a$, KOH-EtOH , and $\text{NH}_3\text{-EtOH}$.

IV. The benzoylation of *syn*- and *anti*-3 : 4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ and *anti*-*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ has been studied with the following results. *anti*-Aldoximes (IV) with BzCl in presence of aq. alkali give Bz derivatives of the *syn*-forms, but in presence of alkali in aq. dioxan (solution or emulsion) they give nitriles. With BzCl in $\text{C}_5\text{H}_5\text{N}$, (IV) give largely or entirely nitriles; in presence of NEt_3 nitrile is obtained. *syn*-Aldoximes (V) with BzCl in $\text{C}_5\text{H}_5\text{N}$ give partly or entirely nitriles but, in presence of NEt_3 , give entirely Bz derivatives of (V). It is concluded that although changes of configuration may occur under certain conditions, no such change occurs when either (IV) or (V) are benzoylated in a sufficiently basic solution.

H. W.

Preparation of α -alkyl- and α -acyl-phenylhydrazones, and α -alkylphenylhydrazines. P. GRAMMATIKAKIS (Compt. rend., 1939, 209, 994—997).— $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$ with NaNH_2 in Et_2O or C_6H_6 gives $\text{CHPh}\cdot\text{N}\cdot\text{NNaPh}$ (I) which with MeI gives benzaldehydephenylmethylhydrazone (II), b.p. 212—213°/15

mm., m.p. 104°, hydrolysed (HCl) to PhCHO , $\text{NH}_2\cdot\text{NPhMe}$, and a small amount of $\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NHMe})_2$ formed by decomp. of (II) to PhCHO and NHPhMe followed by interaction of these compounds. (II) with MgMeI gives acetophenoneimine, b.p. 93°/12 mm. (phenylcarbamyl derivative, m.p. 160°), and NHPhMe . Similarly (I) with EtI , Bu^tI , and CH_2PhCl gives benzaldehydephenyl-ethyl-, b.p. 214°/14 mm., m.p. 50°, -isobutyl-, b.p. 219—220°/13 mm., and -benzyl-hydrazone, m.p. 111°, respectively, hydrolysed to PhCHO and $\text{NPhAlk}\cdot\text{NH}_2$. (I) with BzCl and AcCl gives benzaldehyde-benzoyl-, m.p. 123°, and -acetyl-phenylhydrazone, m.p. 122°, which when hydrolysed do not yield the appropriate acyl-phenylhydrazines. J. L. D.

Associating effect of the hydrogen atom. V. Nitroarylhydrazones. L. HUNTER and J. A. MARRIOTT (J.C.S., 1940, 166—170; cf. A., 1939, II, 214).—Cryoscopic measurements of the mol. wts. of NO_2 -substituted arylhydrazones over a range of concn. provide direct evidence of H-bond association. There are thus two kinds of H-bond association: (i) homogeneous, between typical associating groups of the same kind, as in phenols, oximes, amides; (ii) heterogeneous, between electron-donor and -acceptor groups of different kinds, e.g., $\cdot\text{NO}_2\cdots\text{HO}\cdot$, $\cdot\text{NO}_2\cdots\text{HNAr}\cdot\text{N}\cdot$ (A). A high degree of mol. association occurs in nitroarylhydrazones whenever NO_2 and $\text{NHAr}\cdot\text{N}\cdot$ in separate mols. are free to unite by means of a H bond, viz., (A). $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$ is weakly associated. Substitution of NO_2 in either Ph nucleus, e.g., *o*-, *m*-, or *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ (much less associated in C_{10}H_8 than in *p*- $\text{C}_6\text{H}_4\text{Br}_2$ owing to compound formation with C_{10}H_8 ; *p*- $\text{C}_6\text{H}_4\text{Br}_2$ is generally used) or $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ -*p* (in C_{10}H_8), causes a high degree of association. $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ -*o* in which intramol. H bonding can occur is unassociated. *o*-, *m*-, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NRPh}$ ($\text{R} = \text{Me}$ or Ph) are all unassociated. *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh}$ is associated, but *m*-nitroacetophenonediphenylhydrazone, m.p. 105°, is unassociated. Association is checked with $\text{CPhMe}\cdot\text{N}\cdot\text{NRPh}$ ($\text{R} = \text{H}$ or Ph). In C_{10}H_8 solution, *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ -*o* is unassociated; both H of OH and NH are chelated. The *p*- NO_2 -isomeride is associated (as A). Other substituted arylhydrazones are investigated. Conclusions as to mol. association are based not on abs. vals. of the association factor, but on the slope of the association-concn. curves; a steep curve indicates a high, and a flat or gently-sloped curve a low, degree of association. F.p. systems showing compound formation are: C_{10}H_8 -*p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ (I), unstable 1 : 1 compound, m.p. 123°, eutectic point for mixtures rich in C_{10}H_8 at 77°, and eutectic arrest for mixtures rich in (I) at 113°; C_{10}H_8 -*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, unstable 1 : 1 compound, m.p. 85°, eutectic point (40% by wt. of C_{10}H_8) at 67°. $\text{CHPh}\cdot\text{N}\cdot\text{NPhMe}$ has m.p. 106° (lit. 102°). A. T. P.

1 : 2 : 2-Trimethylcyclopentane-1 : 3-dialdehyde, "camphoecandialdehyde." F. HÄFLIGER (Helv. Chim. Acta, 1940, 23, 90—92).—Camphor glycol and $\text{Pb}(\text{OAc})_4$ in $\text{C}_6\text{H}_6\text{-AcOH}$ at 35—40° give

63% of 1 : 2 : 2-trimethylcyclopentane-1 : 3-dialdehyde, m.p. $\sim 97^\circ$, b.p. $120\text{--}122^\circ/12\text{ mm.}$, $[\alpha]_D^{20} + 95\text{--}13^\circ$ in C_6H_6 [disemicarbazone, m.p. 230° (decomp.); di-*p*-nitrophenylhydrazone, m.p. 239°]. R. S. C.

Synthesis of 2-acylresorcinols by the "Nidhon" process. VI. 2-*n*-Valeryl- and -*m*-toluoyl-resorcinol. V. K. BHAGWAT and R. Y. SHAHANE (Rasāyanam, 1939, 1, 191—194; cf. Limaye, A., 1934, 298).—*n*-Valeryl chloride and 4-methylumbelliferone at $90\text{--}130^\circ$ give the *n*-valerate, m.p. 77° , converted by AlCl_3 at 165° into 8-*n*-valeryl-4-methylumbelliferone (I), m.p. 106° (benzoate, m.p. 113°), and this with 20% aq. NaOH in H_2 affords 2-*n*-valerylresorcinol (II), m.p. 85° [with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ and H_2SO_4 gives (I); diacetate; Me_2 ether, b.p. $172\text{--}175^\circ/15\text{ mm.}$]. The mother-liquors from (I) gave material, which with boiling 20% aq. NaOH in H_2 affords some (II), 6-*n*-valeryl-4-methylumbelliferone, m.p. 157° (acetate, m.p. 153°), and 2 : 4-dihydroxy-5-*n*-valeryl-β-methylcinnamic acid, m.p. 146° . 4-Methylumbelliferone *m*-toluate, m.p. 146° , and AlCl_3 at $160\text{--}165^\circ$ give 8-*m*-toluoyl-4-methylumbelliferone, m.p. 233° (acetate, m.p. 163° ; benzoate, m.p. 157° ; Me ether, m.p. 184°), and thence 2-*m*-toluoylresorcinol, m.p. 145° (dibenzoate, m.p. 101° ; Me_2 ether, m.p. 103°). *m*-Toluic acid, $\text{m-C}_6\text{H}_4(\text{OH})_2$, and ZnCl_2 at 140° give 4-*m*-toluoylresorcinol (III), m.p. 168° (diacetate, m.p. 73°), which does not condense with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}\cdot\text{H}_2\text{SO}_4$. (III) and $\text{Ac}_2\text{O}\cdot\text{NaOAc}$ at $160\text{--}165^\circ$ afford, after hydrolysis with *N*-NaOH of its acetate (IV), m.p. 114° , 4-*m*-tolylumbelliferone, m.p. 223° . (IV) and AlCl_3 at $140\text{--}145^\circ$ give 8-*acetyl*-4-*m*-tolylumbelliferone, m.p. 132° , hydrolysed (NaOH) to 2 : 6 : 1- $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{COMe}$ and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$. A. T. P.

γ-Substitution in the resorcinol nucleus. V. Gattermann reaction with 4-acylresorcinols. H. A. SHAH and R. C. SHAH (J.C.S., 1940, 245—247; cf. A., 1939, II, 373).—Resorpiophenone, $\text{Zn}(\text{CN})_2$, and KCl in EtOAc followed by $\text{AlCl}_3\cdot\text{HCl}\cdot\text{Et}_2\text{O}$ give 2 : 4-dihydroxy-3-aldehydopropiophenone (I), m.p. $140\text{--}141^\circ$ [2 : 4-dinitrophenylhydrazone, m.p. $265\text{--}267^\circ$ (decomp.)]. 2-Methylresorcinol (II) and $\text{EtCN}\cdot\text{HCl}\cdot\text{ZnCl}_2\cdot\text{Et}_2\text{O}$ give 2 : 4-dihydroxy-3-methylpropiophenone, m.p. $128\text{--}130^\circ$, reduced (Clemmensen) to 2-methyl-4-propylresorcinol (III), m.p. $102\text{--}103^\circ$, obtained also by Clemmensen reduction of (I). $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ and (III) in 80% H_2SO_4 give 7-hydroxy-4 : 8-dimethyl-6-propylcoumarin, m.p. $160\text{--}162^\circ$. $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ (+ piperidine) or $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (+ 20% aq. NaOH) and (I) give 5-hydroxy-3-acetyl-6-propionylcoumarin, m.p. $188\text{--}190^\circ$, or 5-hydroxy-6-propionylcoumarin-3-carboxylic acid, m.p. $185\text{--}186^\circ$ (decomp.), respectively. Resbutyrophenone similarly affords 2 : 4-dihydroxy-3-aldehydobutyrophenone (IV), m.p. $42\text{--}43^\circ$ [semicarbazone, m.p. $242\text{--}245^\circ$ (decomp.)]. (II), as above, affords 2 : 4-dihydroxy-3-methylbutyrophenone, m.p. $155\text{--}157^\circ$, reduced (Clemmensen), as is (IV), to 2-methyl-4-butyresorcinol, m.p. $74\text{--}76^\circ$. (IV) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ give 5-hydroxy-6-butyrylcoumarin-3-carboxylic acid, m.p. $198\text{--}200^\circ$ (decomp.). 2 : 4 : 1- $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{COPh}$ gives 2 : 4-dihydroxy-3-aldehydobenzophenone (V), m.p. $117\text{--}118^\circ$ [2 : 4-dinitrophenylhydrazone, m.p. $228\text{--}230^\circ$ (decomp.)], reduced (Clemmensen) to 4-benzyl-2-methylresorcinol, m.p.

$96\text{--}98^\circ$, also obtained similarly from 2 : 4 : 3 : 1- $(\text{OH})_2\text{C}_6\text{H}_2\text{Me}\cdot\text{COPh}$ (cf. Jones *et al.*, A., 1932, 852). (V) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ give 5-hydroxy-6-benzoylcoumarin-3-carboxylic acid, m.p. 244° (decomp.). 2 : 4 : 1- $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ gives 2 : 4-dihydroxy-3-aldehydophenyl benzyl ketone (VI), m.p. $110\text{--}112^\circ$ [2 : 4-dinitrophenylhydrazone, m.p. $252\text{--}253^\circ$ (decomp.)]; semicarbazone, m.p. $248\text{--}249^\circ$ (decomp.)]. (II) and $\text{CH}_2\text{Ph}\cdot\text{CN}\cdot\text{ZnCl}_2\cdot\text{HCl}\cdot\text{Et}_2\text{O}$ give 2 : 6-dihydroxy-*m*-tolyl benzyl ketone, m.p. $157\text{--}159^\circ$, reduced (Clemmensen), as is (VI), to 4-β-phenylethyl-2-methylresorcinol, m.p. $115\text{--}116^\circ$ (di-*p*-nitrobenzoate, m.p. $140\text{--}142^\circ$). (VI) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{CH}_2(\text{CO}_2\text{Et})_2$ (+ piperidine), or $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ give 5-hydroxy-6-phenylacetylcoumarin-3-carboxylic acid, m.p. $215\text{--}217^\circ$ (decomp.), its *Et* ester, m.p. $200\text{--}201^\circ$, or 5-hydroxy-6-phenylacetyl-3-acetylcoumarin, m.p. $198\text{--}200^\circ$, respectively. A. T. P.

(A) Condensation of *p*-anisylsuccinic anhydride with anisole and tolyl methyl ethers. G. A. DALAL, K. V. BOKIL, and K. S. NARGUND. (B) Condensation of *p*-anisylsuccinic anhydride with the methyl ethers of pyrocatechol, resorcinol, and quinol. G. S. SAVKAR, K. V. BOKIL, and K. S. NARGUND. (C) Condensation of succinic anhydride with the methyl ethers of orcinol and pyrogallol. G. A. DALAL, K. V. BOKIL, and K. S. NARGUND (J. Univ. Bombay, 1939, 8, Part 3, 190—197, 198—202, 203—204).—(A) Condensation (AlCl_3) of PhOMe with *p*-anisylsuccinic anhydride (I) gives γ-keto-α-γ-di-*p*-anisylbutyric acid (II), m.p. 163° (Ag salt; Me , m.p. 98° , and *Et* ester, m.p. 85°), the yield in $\text{C}_2\text{H}_5\text{Cl}_4$ (a little of a substance, m.p. 83° , also formed) is $>$ in $\text{PhNO}_2 >$ in CS_2 . *p*-Anisyl-*p*-methoxystyryl ketone and Br in CS_2 give the dibromide (III), m.p. 150° (slight decomp.), which with EtOH-KCN and subsequent hydrolysis gives (II). Similarly *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ and (I) yield γ-keto-α-*p*-anisyl-γ-6-methoxy-*m*-tolylbutyric acid (IV), m.p. 170° (Ag salt; Me , m.p. 98° , and *Et* ester, m.p. 82°), the effect of solvents being similar. Methylation (Me_2SO_4 , 10% NaOH) of 3 : 1-4- $\text{C}_6\text{H}_3\text{MeAc}\cdot\text{OH}$ gives 4-methoxy-3-methylacetophenone, b.p. $260\text{--}265^\circ$, from which 6-methoxy-*m*-tolyl *p*-methoxystyryl ketone, an oil, and its dibromide, m.p. 121° , were prepared as for (III) but did not react with KCN. 1 : 3 : 6- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{OH}$ gives by methylation 3-bromo-6-methoxytoluene, b.p. $110\text{--}115^\circ/10\text{ mm.}$, which with Mg and Et_2O (Grignard) followed by (I) yields (IV). *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ and (I) give γ-keto-α-*p*-anisyl-γ-5-methoxy-*o*-tolylbutyric acid (V), m.p. 148° (Ag salt; Me ester, b.p. $210\text{--}215^\circ/8\text{ mm.}$), the effect of solvents on the yield being similar. 2 : 1 : 4- $\text{C}_6\text{H}_3\text{MeAc}\cdot\text{OMe}$ and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (VI) in EtOH with NaOH yield 5-methoxy-*o*-tolyl *p*-methoxystyryl ketone, m.p. 147° , the dibromide, m.p. 160° , of which with EtOH-KCN gives (V). *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ in a similar way provides γ-keto-α-*p*-anisyl-γ-4-methoxy-*m*-tolylbutyric acid (VII), m.p. 168° (Me , b.p. $250^\circ/18\text{ mm.}$, and *Et* ester, m.p. 95°). Methylation of 5 : 1-2- $\text{C}_6\text{H}_3\text{MeAc}\cdot\text{OH}$ yields 2-methoxy-5-methylacetophenone, b.p. 254° , $120^\circ/8\text{ mm.}$, which does not give a chalcone with (VI). (VII) was synthesised from (I) and the Grignard reagent from 1 : 3 : 4- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{OMe}$. Pyrylium derivatives are formed

from (II), (IV), (V), and (VII) with o -OH-C₆H₄-CHO in MeOH-HCl.

(B) Guaiacol does not react, but o -C₆H₄(OMe)₂ and (I) give γ -keto- α - p -anisyl- γ -3:4-dimethoxyphenylbutyric acid (VIII), m.p. 188° (Ag salt; semicarbazone, m.p. 176°; Me, m.p. 138°, and Et ester, m.p. 88°); the dibromide, m.p. 138°, of 3:4-dimethoxyphenyl p -methoxystyryl ketone with KCN and subsequent hydrolysis yields (VIII). m -C₆H₄(OMe)₂ gives γ -keto- α - p -anisyl- γ -2:4-dimethoxyphenylbutyric acid (IX), m.p. 201° (Ag salt; Me, m.p. 107°, and Et ester, m.p. 112°; semicarbazone, m.p. 211°). In this case the yield in CS₂ is > in PhNO₂ > in C₂H₂Cl₄. 1:2:4-C₆H₃Ac(OMe)₂ and (VI) in EtOH with NaOH give 2:4-dimethoxyphenyl p -methoxystyryl ketone, m.p. 86°, the dibromide, m.p. 118°, of which with KCN affords no cryst. product. (I) with the Grignard reagent from 4:1:3-C₆H₃I(OMe)₂ gives (IX). m -OMe-C₆H₄-OH gives γ -keto- α - p -anisyl- γ -2-hydroxy-4-methoxyphenylbutyric acid, m.p. 169° (Ag salt; Me, m.p. 92°, and Et ester, m.p. 111°; semicarbazone, m.p. 157°), the yield in C₂H₂Cl₄ is > in PhNO₂ > in CS₂; on methylation it yields (IX). p -OMe-C₆H₄-OH does not react, but p -C₆H₄(OMe)₂ gives γ -keto- α - p -anisyl- γ -2:5-dimethoxyphenylbutyric acid (X), m.p. 168° (Me, m.p. 102°, and Et ester, m.p. 75°; semicarbazone, m.p. 126°). The yield in PhNO₂ is > in C₂H₂Cl₄; no reaction occurs in CS₂. 1:2:5-C₆H₃Ac(OMe)₂ and (VI) in EtOH with NaOH yield 2:5-dimethoxyphenyl p -methoxystyryl ketone, m.p. 99°, the dibromide, m.p. 112°, of which with KCN and subsequent hydrolysis gives (X).

(c) 1:3:5-C₆H₃Me(OMe)₂ with (CH₃CO)₂O and AlCl₃ (cf. A., 1937, II, 500) yields γ -keto- γ -2:4-dimethoxy-6-methylphenylbutyric acid (XI), m.p. 120° (Me, b.p. 160°/16 mm., and Et ester, b.p. 170°/20 mm.). 3:1:5-OH-C₆H₃Me-OMe gives γ -keto- γ -4-hydroxy-2-methoxy-6-methylphenylbutyric acid, m.p. 145° (Ag salt), which is methylated to (XI). 1:2:3-C₆H₃(OMe)₃ gives γ -keto- γ -2-hydroxy-3:4-dimethoxyphenylbutyric acid (Me, m.p. 110°, and Et ester, m.p. 58°; semicarbazone, m.p. 185°). The yields in CS₂, PhNO₂, and C₂H₂Cl₄ are recorded. F. R. G.

β -Arylglutaconic acids. V. α -C-Diacetylation of β -arylglutaconic anhydrides: new method of synthesis of diphenyl derivatives. G. R. GOGTE (J. Univ. Bombay, 1939, 8, Part 3, 208—219).— β - p -Anisylglutaconic anhydride with NaOAc and Ac₂O yields an α -Ac₂ derivative, m.p. 108° (compound, C₂₂H₂₁O₆N, m.p. 144°, with NH₂Ph), which with aq. HCl gives p -OMe-C₆H₄-CMe:CH₂ or p -OMe-C₆H₄-C<CH-CO>O, and with 10% NaOH gives 3'-hydroxy-4-methoxy-5'-methylidiphenyl (I), m.p. 118° (benzoate, m.p. 120°), together with its 2'-carboxylic acid (II), m.p. 182° (decomp.), which with boiling dil. HCl gives (I). 3- p -Anisyl-5-methyl- Δ^5 -cyclohexenone is oxidised by aq. EtOH-FeCl₃ to (I). (II) heated at 200°/40 mm. gives the ester, m.p. 119°, of (I) with (II). Similarly β -2-methoxy-5-methylphenylglutaconic anhydride yields its α -Ac₂ derivative, m.p. 168°, which with boiling conc. HCl gives β -acetonyl-2-methoxy-5-methylcinnamic acid, and with 10% NaOH gives 3'-hydroxy-2-methoxy-5:5'-dimethyldiphenyl

(III), m.p. 85° (acetate, b.p. 181—185°/6 mm.), together with its 2'-carboxylic acid (IV), m.p. 213° (decomp.) [acetate, m.p. 161°; ester, m.p. 127°, with (III)], and 6'-carboxylic acid (V), m.p. 192° (decomp.). (IV) with conc. H₂SO₄ gives the lactone, m.p. 194° (acetate, m.p. 163°), of 2:3'-dihydroxy-5:5'-dimethyldiphenyl-2'-carboxylic acid together with 1-hydroxy-5-methoxy-3:8-dimethylfluorenone, m.p. 168° (acetate, m.p. 191°). Similarly (V) gives 3-hydroxy-5-methoxy-1:8-dimethylfluorenone, m.p. 264° (acetate, m.p. 172°). β -4-Methoxy-3-methylphenylglutaconic anhydride similarly gives an α -Ac₂ derivative, m.p. 158° (decomp.), which with 10% NaOH gives 3'-hydroxy-4-methoxy-5:5'-dimethyldiphenyl, m.p. 69°, and its 2'-carboxylic acid, m.p. 172° (decomp.).

F. R. G.

Attempted synthetic preparation of anti-rachitic vitamins. IV. Preparation of 4-hydroxycyclohexanone. K. DIMROTH (Ber., 1939, 72, [B], 2043—2051).—Partial hydrolysis of quinitol diacetate (*cis* + *trans*) with NaOEt-EtOH gives a mixture of *cis*- and *trans*-diols and their mono- and diacetates which are inseparable by fractional distillation but can be extracted with various solvents, leading thus to *trans*-(I), m.p. 72—73°, and *cis*-(II), an oil, 4-hydroxycyclohexyl acetate, which closely resembles (I) in its properties. (I) and (II) give 3:5-dinitrobenzoates (III) and (IV), m.p. 145—146° and 119—122°, respectively. (III) is hydrolysed by 2N-H₂SO₄-EtOH at 100° to *trans*-4-hydroxycyclohexyl 3:5-dinitrobenzoate, m.p. 150—151°, and thence by KOH-MeOH to *trans*-cyclohexane-1:4-diol whilst (IV) gives the corresponding *cis*-3:5-dinitrobenzoate, m.p. 118—121°, and thence *cis*-cyclohexane-1:4-diol. *trans*-4-Hydroxycyclohexyl benzoate has m.p. 86—87°. Oxidation of a mixture of (I) and (II) in C₆H₆ by CrO₃ in aq. AcOH at 75—80° gives a mixture (A) of unchanged material and 4-acetoxycyclohexanone (V), b.p. 117—119°/12 mm. (? 3:5-dinitrophenylhydrazones, m.p. 184.5°). (V) gives a semicarbazone, m.p. 185—186°, from which it is not smoothly regenerated by H₂C₂O₄ or H₂SO₄ by reason of the susceptibility of OAc. The best method of separating (V) from (A) is by decomp. of the H sulphite by dil. H₂SO₄ under Et₂O but the yields of the cryst. salt are not satisfactory. (V) is hydrolysed by 2N-H₂SO₄ at 100° to 4-hydroxycyclohexanone, b.p. 128—131°/12.5 mm. (? 3:5-dinitrophenylhydrazones, m.p. 151°). Quinol is readily converted by AcCl in well-cooled C₅H₅N into the monoacetate, b.p. 160—162°/11 mm., m.p. 62—63°.

H. W.

2:3-Diphenyl- Δ^2 -cyclopentenone. W. BORSCHÉ and A. KLEIN (Ber., 1939, 72, [B], 2082).—Cyclisation of Et α -phenacyl- γ -phenylacetoacetate by warm 2% NaOH affords 2:3-diphenyl- Δ^2 -cyclopentenone, b.p. 185—190°/1 mm., m.p. 95°, in ~80% yield. It gives a 2:4-dinitrophenylhydrazones, m.p. 226°, a 5-CHPh⁺, m.p. 158°, and 5- p -anisylidene, m.p. 159°, derivative.

H. W.

Naphthylacrylic acids and their derivatives. II. Ring-closure. A. BANCHETTI (Gazzetta, 1939, 69, 809—816).— β -2-Naphthylcrotonic acid of m.p. 170° (I) or 142° (II) (A., 1939, II, 423) with H₂SO₄ gives sulphonic acids, without ring-closure; (I) is little

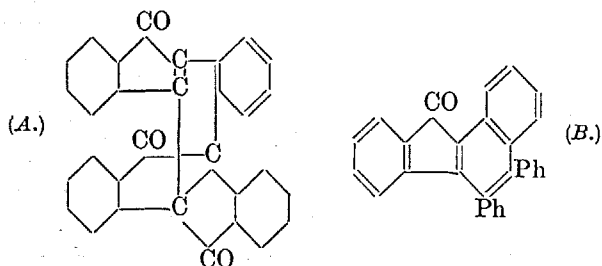
affected by P_2O_5 . The acid chloride from (I) with $AlCl_3$ gives amorphous products. The Et ester with P_2O_5 in C_6H_6 gives $2-C_{10}H_7Ac$ (III); in xylene, products, m.p. 260–264°, and ~170°, are formed. β -2-Naphthylbutyryl chloride with $AlCl_3$ gives 3-methyl-5:6-benzo-1-hydrindone, m.p. 73–73.5° [semicarbazone, m.p. 203–205° (block) (decomp. to a product, m.p. ~220°); oxime not obtained]. A by-product of the prep. of (I) from (III) is a compound, ? $(C_7H_6O)_3$ (formation of which is difficult to explain), m.p. 103–104°, whilst the crude Reformatsky product from (III) contains a substance, $C_{26}H_{18}O$, m.p. 208–210°.

E. W. W.

3:3-Diphenyl-1-hydrindone and 3:3-diphenylindane-1:2-dione. Synthesis of *o*-benzhydrylbenzoylformic acid. P. E. GAGNON, R. HUDON, I. CANTIN, and J. GANAS (Trans. Roy. Soc. Canada, 1939, [iii], 33, III, 47–58).—3:3-Diphenyl-1-hydrindone (I) (A., 1930, 90) with boiling aq. $KOH-KMnO_4$ gives diphenylphthalide (II). With HNO_3 (d 1.2), (I) gives a mixture (III) [containing (II)] which in C_6H_6 with NH_3 deposits the NH_3 compound, $C_{21}H_{17}O_5N_3$, m.p. 170–171° (decomp., evolving NH_3), of 2:2-dinitro-3:3-diphenyl-1-hydrindone, m.p. 190–192° (decomp.), liberated by Ac_2O . When heated at 160° under reduced pressure, (III) gives 3:3-diphenylindane-1:2-dione (IV) (cf. Schönberg *et al.*, A., 1937, II, 248) (mono-oxime, m.p. 100–110°, -hydrazone, m.p. 163–164°, -phenylhydrazone, m.p. 186–188°, -p-nitrophenylhydrazone, m.p. 238–240°). With PCl_5 and PBr_5 , (IV) gives 1:1-dichloro-, m.p. 134–135°, and 1:1-dibromo-3:3-diphenyl-2-hydrindone, m.p. 110–115° (structure deduced from non-identity with the known 2:2:3:3:1-compound). With *o*- $C_6H_4(NH_2)_2$, (IV) gives 2-*o*-aminoanilo-3:3-diphenyl-1-hydrindone, m.p. 241–242°. When heated with $AcOH$ for 10 hr., (III) gives (II) and (IV). (IV) is converted by boiling conc. aq. KOH [if the solution is then saturated with CO_2 , any (II) present is pptd.] into *o*-benzhydrylbenzoylformic acid (V), m.p. 224–226° (N_2H_4 salt, m.p. ~205°, of hydrazone). The *Ag* salt of (V) gives the *Me* ester, m.p. 93–94°, also obtained via the acid chloride; the last with conc. aq. NH_3 followed by $EtOH$ gives the *Et* ester, m.p. 69–70°, not the amide. $KOH-H_2O_2$ oxidises (V) to *o*- $CHPh_2-C_6H_4-CO_2H$.

E. W. W.

Diphensuccindene series. XVII. Δ^{10} -Diphensuccindene-9:12-dione. K. BRAND and H. W. STEPHAN (Ber., 1939, 72, [B], 2168–2175; cf. A., 1937, II, 24).—Evidence is adduced in favour of the constitution (A) for the red compound (I),



$C_{31}H_{16}O_3$, obtained (*loc. cit.*) by dehydrogenation of diphensuccindane-9:12-dione by SeO_2 . (I) is

smoothly oxidised by CrO_3 in $AcOH$ to products of unknown constitution. Gradual addition of (I) to hot, 10% $KOH-EtOH$ gives a neutral substance, $C_{31}H_{18}O_4$, m.p. 312–313.5° (converted by the protracted action of $KOH-EtOH$ into a compound sol. in Na_2CO_3), and a dicarboxylic acid (II), $C_{31}H_{18(20)}O_5$, m.p. 343–344° (*Me_2* ester, m.p. 216°). (II) is decarboxylated in boiling quinoline containing Cu powder to 5:6-diphenylchrysfluorenone (B), m.p. 247.5–248.5°, which is transformed by molten KOH at 320–330° into a (?) mixture, m.p. 238–243°, of 1:2:3-triphenylnaphthalene-4- and -4'-carboxylic acids, decarboxylated (Cu powder in boiling quinoline) to 1:2:3- $C_{10}H_5Ph_3$, m.p. 152–153.5°. H. W.

Estrogens with oxygen in ring B. II. Δ^6 -isoequilin from 7-hydroxyoestrone. W. H. PEARLMAN and O. WINTERSTEINER (J. Biol. Chem., 1940, 132, 605–612).—A new isomeride of equilin is prepared. Dehydration of 7-hydroxyoestrone by heating with Al_2O_3 is not successful. Its 3-benzoate (A., 1939, II, 511) with $PCl_5-CaCO_3-CHCl_3$ gives 7-chlorooestrone 3-benzoate, m.p. 247–248° (decomp.) (all m.p. corr.), which with NaI in C_5H_5N at 100° for 40 hr. gives, after hydrolysis, Δ^6 -isoequilin (I), m.p. 265–266°, $[\alpha]_D^{25} +150^\circ$ in dioxan (acetate, m.p. 140–141°; benzoate, m.p. 202°), hydrogenated (Pd -black in $EtOH$) to oestrone (II), without any equilinin. C_{28} in the 7-substituted estrogens has thus the same configuration as in natural steroids. (I) has about $\frac{1}{3}$ of the physiological activity of (II). The absorption of (I) shows max. at 263 ($\epsilon = 7500$) and 306 $m\mu$. ($\epsilon = 2500$). The spectra etc. do not agree with those of Inhoffen's isoequilin (A., 1937, II, 147) or of Girard's hippulin (A., 1932, 546). "Compound 3" (Hirschmann *et al.*, A., 1938, III, 299) has an absorption spectrum not completely resembling that of (I), but resembling that of 14-*epi*- Δ^9 -11,8-hydroxyequilin (Hirschmann *et al.*, A., 1939, II, 76).

E. W. W.

17- β -Hydroxyprogesterone. J. J. PIFFNER and H. B. NORTH (J. Biol. Chem., 1940, 132, 459–460).—17- β -Hydroxyprogesterone, m.p. 212–215° (Berl block; uncorr.), $[\alpha]_D^{25} +102 \pm 3^\circ$ in $CHCl_3$, an isomeride of deoxycorticosterone, has been isolated from ox adrenals. It shows an absorption max. at 240 $m\mu$, yields a dioxime, m.p. 250–251° (decomp.; sinters ~240°), and a disemicarbazone, m.p. >360° (darkens 240°, sinters 280–290°), and is unaffected by $Ac_2O-C_5H_5N$ at room temp. Oxidation with CrO_3 in $AcOH$ at room temp. yields Δ^4 -androstene-3:17-dione. It exhibits no progestational or cortical hormone activity, but has a male hormone activity comparable with that of androsterone.

P. G. M.

Constituents of the adrenal cortex and related substances. XXXI. Diazoprogesterone. T. REICHSTEIN and J. VON EUW (Helv. Chim. Acta, 1940, 23, 136–138; cf. A., 1939, II, 553).—21-Diazo- Δ^5 -pregnen-3-ol-20-one and $Al(OBu^r)_3$ in $C_6H_6-COMe_2$, boiling or at room temp. (20 days), give 21-diazoprogesterone, m.p. 182–184° (corr.; decomp.), converted by HCl in dry Et_2O into 21-chloroprogesterone, m.p. 201–204° (corr.) [also obtained from 21-chloropregnenolone by $Al(OBu^r)_3$ in $C_6H_6-COMe_2$

at room temp. (20 days)], and by boiling AcOH into deoxycorticosterone acetate, m.p. 158—159° (corr.).

R. S. C.

Zwitter-ion structures in unsaturated carbonyl compounds.—See A., 1940, I, 148.

Action of nitrosylsulphuric acid on *m*-fluorophenol. A new red *o*-quinoneimine. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1940, 205—207; cf. A., 1939, II, 512; 1940, II, 12).—*m*-C₆H₄F·OH (I) and NO·SO₃H in AcOH at 0—25° give (probably) the red 4:2'-difluoro-4'-hydroxy-*o*-benzoquinone-1-anil (II), m.p. >300°, and a little green 3-fluoro-4-nitrosophenol (or 3-fluorobenzoquinone-4-oxime), m.p. 158° [oxidised by K₃Fe(CN)₆ to 4:3:1-NO₂·C₆H₃F·OH]. (I) is probably nitrosated in position 4 and in small degree nitrated in position 6, followed by rapid condensation of the NO-compound (or quinoneoxime) with (I) to give (II). Boiling aq. KMnO₄-H₂SO₄ and (II) give an odour of a *p*-benzoquinone; Zn-AcOH give a colourless leuco-compound, reoxidised by air or FeCl₃ to (II). (II) or *mm*-difluoro-*o*-indophenol (III) and Zn dust in Ac₂O-NaOAc give 4:2'-difluoro-2:4'- or 4:4'-difluoro-2:2'-diacetoxy-*N*-acetyldiphenylamine, m.p. 175°, respectively. (II) or (III) and NH₂Ph-AcOH give 4:2'-difluoro-4'-, m.p. 200°, or 4:4'-difluoro-2'-hydroxy-*o*-benzoquinonedianil, m.p. 175°, respectively.

A. T. P.

Examination and determination of 2-methyl-1:4-naphthaquinone. J. L. PINDER and J. H. SINGER (Analyst, 1940, 65, 7—12).—Volumetric determination is carried out by titration with TiCl₃ in CO₂ using K indigodisulphonate or phenosafranine as internal oxidation-reduction indicator. The colour reaction between CN·CH₂·CO₂Et and quinones in aq. NH₃-EtOH (Craven, A., 1931, 972) was studied and successfully applied to the colorimetric determination of 0.4—0.8 mg. and to EtOH extracts of tablets, pills, and ampoules. Spectrographic absorption data and control tests for ash, m.p., loss on drying in vac., and Cr content are given.

E. C. B. S.

Biochemistry of micro-organisms. LXIV. Emodic (4:5:7-trihydroxyanthraquinone-2-carboxylic) acid and ω -hydroxyemodin (4:5:7-trihydroxy-2-hydroxymethylanthraquinone), metabolic products of a strain of *Penicillium cyclopium*, Westling. W. K. ANSLOW, J. BREEN, and H. RAISTRICK (Biochem. J., 1940, 34, 159—168).—The mycelium of a strain of *P. cyclopium*, grown on a Raulin-Thom solution at 20—21° in daylight, when extracted with Et₂O + 2N-HCl gives emodic acid, m.p. 364—365° (decomp.) (smokes ~350°) [*Me* ester, m.p. 268—270° (triacetate, m.p. 188—189°)], and 4:5:7-trihydroxy-2-hydroxymethylanthraquinone (I), m.p. 288° [tetra-acetate (II), m.p. 190—191°; 7-*Me* ether, m.p. 229—231° (prep. by MeI in MeOH-NaOMe; insol. in cold 2% aq. Na₂CO₃)], separated through their polyacetates. (I) is sol. in cold N-Na₂CO₃ but insol. in cold 2% aq. NaHCO₃. Reduction of (I) with red P and HI (*d* 1.7) in boiling AcOH and subsequent oxidation (CrO₃, aq. AcOH, 60°) of the resulting anthranol, decomp. 255—258° (darkens 250—255°), affords *Frangula*-emodin [4:5:7-

trihydroxy-2-methylanthraquinone] (III). Oxidation (CrO₃, aq. AcOH, 65—70°) of (II) or the triacetate of (III) gives triacetylemodic acid. The compound, C₁₅H₁₀O₆, m.p. 273°, of Posternak (A., 1939, III, 872) is (I). H. B.

Preparation of 1:3-dihalogeno-2-methylaminoanthraquinones.—See B., 1940, 192.

Vat dyes of the flavanthrone series. III. T. MAKI and S. KITAMURA (J. Soc. Chem. Ind. Japan, 1939, 42, 410—412B).—2-Bromo-3-aminoanthraquinone (I) (3 g.) is gradually added to SbCl₅ (8.5 g.) in PhNO₂ (50 g.) at 20°; the mixture is kept for ~18 hr. with exclusion of moisture, then heated as rapidly as possible to 210° and kept at this temp. for 15—20 min. The ppt. is removed at ~140°, washed with PhNO₂ at ~100° and then with EtOH, after which it is boiled with 10% HCl, thus giving 3:3'-dibromoflavanthone (II) in 33.1% yield. (II) gives a violet-blue vat with alkaline Na₂S₂O₄ at 55—60° from which cotton is dyed in brilliant yellow-orange shades. It is not identical with indanthrene-yellow R. If the time of condensation has been shortened the filtrates from (II) contain almost homogeneous 3:3'-dibromindanthrone (III). If the change has been prolonged a yellow-green substance, probably 3-bromo-3'-(3''-bromo-2''-anthraquinonylamino)indanthrone, accompanies (II). A 1:1:1 compound (IV) of (I), SbCl₅, and PhNO₂ is described. If C₆H₄Cl₂ is used as solvent, no (II) and only traces of (III) are formed. A compound analogous to (IV) is not observed. H. W.

Walden inversion. IV. Mode of reaction of phosphorus pentachloride. W. HÜCKEL and H. PIETRZOK (Annalen, 1939, 540, 250—274; cf. A., 1939, II, 120).—*l*-Menthol (I) (=ROH) (~1 mol.) in C₅H₅N (best 4 mols.) and PCl₅ (~1 mol. in cold light petroleum) give a poor yield of almost homogeneous *d*-neomenthyl chloride [3^c-chloro-1^c-methyl-4^c-isopropylcyclohexane] (II), b.p. 40—41°/0.01 mm., [α]_D²⁰ +44.72°, with much trimethyl orthophosphate, m.p. 84°, and Cl-containing phosphates. Reaction is considered to involve [C₅H₅N·PCl₄]⁺Cl⁻ (in this and similar formulae : denotes a lone pair of electrons) or [(C₅H₅N)₂·PCl₄]⁺Cl⁻; OH is then substituted by Cl⁻ with complete Walden inversion (cf. A., 1939, II, 147). Interaction between (I) and [C₅H₅N·PCl₄]⁺ can also occur: $\left[\begin{smallmatrix} R \\ H \end{smallmatrix} \right] > O : P(Cl_4) : NC_5H_5 \right]^+ \rightarrow [C_5H_5NH]^+ + RO : PCl_4$ (with C₅H₅N gives [RO : P(Cl₃) : NC₅H₅]⁺Cl⁻). With unpurified PCl₅ in cold light petroleum, (I) affords mixtures (4), [α]_D²⁰ -25° to -30°, of (II) and much *l*-menthyl chloride [3^c-chloro-1^c-methyl-4^c-isopropylcyclohexane] (III); use of pure PCl₅ (also in Et₂O, CCl₄, and CHCl₃) gives mixtures of (II) (increased amount) and (III). With PCl₅ containing increasing amounts of FeCl₃ (or AlCl₃), chlorides of increasing laevorotatory power are formed; a 1:1:1 mixture of (I), PCl₅, and FeCl₃ in light petroleum gives practically pure (III), α_D -37.3°, and a little menthene. In this case interaction is considered to occur thus: $[PCl_4]^+[FeCl_4]^- + ROH \rightarrow \left[\begin{smallmatrix} R \\ H \end{smallmatrix} \right] > O : PCl_4 \right]^+[FeCl_4]^- \rightarrow RCl + POCl_3 + H^+ + [FeCl_4]^-$; no inversion occurs and there is no conversion (by FeCl₃ or PCl₅-FeCl₃) of

(II) into (III). Formation of (II) and (III) is not concerned with the HCl liberated during the reactions; (I) is unaffected by dry HCl in Et₂O or C₆H₆ at room temp./8 weeks. Conc. HCl and (I) at 100° (sealed tube) give a mixture of (II) (25%) and (III) (75%). The reaction between (I) and PBr₅ is similarly influenced by AlBr₃ (e.g., $\frac{1}{15}$ mol. leads to a *bromide*, b.p. 44–46°/0.005 mm., $[\alpha]_D^{20} -20.14^\circ$); pure PBr₅ affords a *bromide*, $[\alpha]_D^{20} -3.93^\circ$ to $+7.67^\circ$, and some *dibromomenthane*, b.p. 80°/0.008 mm. [probably from menthone which arises by oxidation of (I)].

Quinoline at 190–200° or, less well, NH₂Ph at 160–170° with (A) gives approx. pure (III) and a mixture of *trans*- Δ^2 - (IV) (15–18%) and active (V) (0–25%) and *r*- Δ^3 -menthene (60–82%); (IV) and (V) are little affected and completely racemised, respectively, by EtOH–C₆H₄Me·SO₃H. The physical consts. of (II) and (III) are in accordance with the von Auwers–Skita rule. The reactions of (I) with those (lit.) of *d*- β -octanol and PCl₅ are compared.

l-Borneol and PCl₅ + FeCl₃ give (method: Wal-lach, A., 1886, 70) *isobornyl chloride* (VI) (largely racemised) formed by way of camphene hydro-chloride (VII); in Et₂O a 3 : 1 mixture of (VI) and (VII) is produced. Pure PCl₅ similarly gives a 1 : 2 mixture of (VI) and (VII).

H. B.

Contact isomerisation of menthene. N. D. ZELINSKI and J. A. ARBUSOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 24, 542–544; cf. A., 1940, II, 9).— Δ^3 -*p*-Menthene (I) passes in presence of SiO₂ gel at 375° mainly into an unsaturated material (II) which is hydrogenated (Pt–C at 170°) and then dehydrogenated (Pd–C at 300°) and treated with fuming H₂SO₄ to remove *p*-cymene. The product is a mixture of pentamethylene hydrocarbons C₁₀H₂₀ formed by hydrogenation of cyclopentene hydrocarbons, C₁₀H₁₈, which are the immediate product of the contact isomerisation of (I). Repeated passage of (II) over Pt–SiO₂ gel at 300° followed by treatment of the condensate with fuming H₂SO₄ leads to a mixture of isomeric decanes.

H. W.

Tricyclal. P. LIPP and H. BRÄUCKER (Ber., 1939, 72, [B], 2079–2081; cf. Jagelki, A., 1899, 1, 627).—Reduction of ω -nitrocamphene by Zn dust and AcOH at 70° affords two alcohols, two aldehydes, and a N compound volatile with steam. The main product is tricyclal, which is identified through the semicarbazone, m.p. 212–212.5° (corr.; decomp.) when slowly heated, and by oxidation to tricyclenic acid, m.p. 150–151°.

H. W.

Optically pure *l*- α -phellandrene. N. C. HANCOX and T. G. H. JONES (Univ. Queensland Papers, 1939, 1, No. 14, 2 pp.).—*l*- α -Phellandrene (I) prepared by fractional distillation at 1–2 mm. in the presence of traces of quinol had $d_D^{20} 0.8324$, $n_D^{20} 1.4724$, $[\alpha]_D^{20} -177.4^\circ$, diene val. ~ 186.3 . A linear relationship was found between $[\alpha]_D$ and the (I) content, calc. from the diene val., for a no. of samples when optically inactive diluents were present.

T. F. W.

Phenolic behaviour of buchu-camphor and its derivatives. (SIGNA.) C. STRANEO (Gazzetta, 1940, 70, 27–37).—Buchu-camphor (I) with Me₂SO₄ in aq. KOH gives its Me ether (II), which with NH₂OH·HCl

gives in presence of NaHCO₃ a NH₂OH derivative, m.p. 106–108°, and in presence of KOH an *oxime*, m.p. 128–131°, with a substance, m.p. 159–161°, b.p. 130–140°/0.1 mm. With NH₂·CO·NH·NH₂, (II) yields two isomeric *pyrazoline* derivatives, C₁₂H₂₁O₂N₃, m.p. 193–194° and 189–192° (mixed m.p. depressed). With Br in Et₂O, (II) gives an unstable product, yielding a small amount of bromo-buchu-camphor, and 2 : 3-dihydroxycymene and its 2-Me ether, m.p. 45–47°. With H₂ (Pd), (II) gives *dihydrobuchu-camphor Me ether* (III), b.p. 222–224°

[*oxime*, m.p. 120–121°; *semicarbazone*, m.p. 197–198° (decomp.)]. With HBr in Et₂O, (III) gives menthone; prolonged action of HBr, followed by 10% KOH, gives Δ^1 -menthen-3-one (?), b.p. (impure) 209–220° (*semicarbazone*, m.p. 146–151°), and some hydroxythymoquinone. Formula (A) is proposed for (II) (R = Me), derived from (I) in a form of structure (A) (R = H).

E. W. W.

Formation of mixed crystals or molecular compounds from binary systems of keto-derivatives of camphor.—See A., 1940, I, 164.

Camphorquinone and diazomethane. H. RUPE and F. HÄFLINGER (Helv. Chim. Acta, 1940, 23, 139–143).—Camphorquinone and CH₂N₂ in C₆H₆ containing a little MeOH, first at 0° and then at room temp., give a *ketone* (I), C₁₁H₁₅O·OMe, m.p. 55–56°, b.p. 145°/12 mm. (*perchlorate*, m.p. 90°; *oxime*, m.p. $\sim 195^\circ$), and a liquid mixture, which with 10% HCl at 100° yields an *acid* (II), C₁₁H₁₆O₂, m.p. $\sim 220^\circ$ [*phenylurethane*, m.p. 91°; *Br-derivative*, m.p. 191°, reduced to (II) by Zn dust in AcOH]. Hot 20% H₂SO₄ converts (I) into (II) and MeOH. MeOH–H₂SO₄ converts (II) into (I), which is also obtained from the Ag salt of (II) by MeI. CrO₃ in aq. AcOH at room temp. oxidises (II) to camphoric acid; H₂–Ni at 70°/120 atm. reduces it to *isoborneol*; Na–EtOH reduced it to camphor glycol.

R. S. C.

Autoxidation of *trans*- π -aldehydocamphor. **Influence of other ketocamphors.** M. ISHIDATE and H. KAWAHATA (Proc. Imp. Acad. Tokyo, 1939, 15, 353–356).—2 mols. of 10-ketocamphor entirely stop autoxidation of *trans*- π -aldehydocamphor (I) in a 0.1M-phosphate buffer (p_H 7), probably by complex formation; smaller amounts have less effect. *p*-Ketocamphor (up to 4 mols.) has much less effect. *o*-Ketocamphor is remarkably effective, 0.0025 mol. causing almost complete inhibition. Fe⁺⁺ increases and KCN greatly decreases autoxidation. CuSO₄ in fairly large amount is inhibitory. These results parallel effects on other activities of (I).

R. S. C.

Peroxidase action of π -aldehydocamphor. M. ISHIDATE and F. SHISHIDO (Proc. Imp. Acad. Tokyo, 1939, 15, 357–358).—Addition of a little *trans*- or *cis*- π -aldehydocamphor to $\sim 0.1\%$ *o*-aminophthalhydrazide and 0.03% H₂O₂ in 1% Na₂CO₃ causes prolonged, blue chemiluminescence. KCN, Na₂S, NH₂OH, N₂H₄, *o*- and 10- (but not 6- or *p*-)ketocamphor (1 mol.) inhibit this reaction. 10-Ketocamphor, various aldehydes, and perisoketopinic acid do not cause chemiluminescence.

R. S. C.

Optical superposition. H. RUPE and F. HÄFLINGER (Helv. Chim. Acta, 1940, 23, 53—90).—When a *d*-, *l*-, or *dl*-terpene acid is esterified with a *d*-, *l*-, or *dl*-terpene alcohol, the rules of optical superposition hold unless both components are unsaturated, but the numerical contribution of one component may vary according to the nature of the second. In some cases the effect is overlaid by partial resolution of a *dl*-component by an active component; this is proved by hydrolysis in cases marked * below. Rotatory dispersion (measured) has usually little effect. $[\alpha]$ below are $[\alpha]_D^{20}$ in C_6H_6 . The following are prepared (esters by way of the acid chloride). *dl*- β -Camphorylpropionic acid (from Et camphorylidenepropionate by H_2 -Ni), m.p. 85° [p-toluidide, m.p. 80° (d-acid p-toluidide, m.p. 113°)]. *dl*-Camphorylidene-, m.p. 143° [p-toluidide, m.p. 216° (d-acid p-toluidide, m.p. 215°)], and *dl*-camphoryl-acetic acid, m.p. 115° [p-toluidide, m.p. 140° (d-acid p-toluidide, m.p. 165°)]. Camphorylidenepropionic acid gives no terpene esters. *d*-, m.p. 143°, $[\alpha] + 87.08^\circ$, *l*-, m.p. 133°, $[\alpha] - 90.03^\circ$, and *dl*-hydroxymethylenecamphor *d*-camphorylpropionate, m.p. 139°, $[\alpha] - 0.90^\circ$; *d*-, m.p. 128°, $[\alpha] + 87.00^\circ$, and *l*-hydroxymethylenecamphor *dl*-camphorylpropionate, m.p. 126°, $[\alpha] - 87.48^\circ$. *d*-, m.p. 90°, $[\alpha] + 29.44^\circ$, *l*-, m.p. 113°, $[\alpha] - 2.46^\circ$, and *dl*-camphorylcarbinol *d*-camphorylpropionate, m.p. 94°, $[\alpha] + 11.20^\circ$; *d*-, m.p. 94°, $[\alpha] + 15.33^\circ$, and *l*-camphorylcarbinol *dl*-camphorylpropionate, m.p. 96°, $[\alpha] - 15.22^\circ$; *d*- β -camphorylcarbinol *d*-camphorylpropionate, m.p. 103°, $[\alpha] + 51.03^\circ$. *dl*-Camphorylideneacetyl chloride, b.p. 140—142°/13 mm. *d*-, m.p. 145°, $[\alpha] + 233.57^\circ$, *l*-, m.p. 121°, $[\alpha] + 1.68^\circ$, and *dl*-hydroxymethylenecamphor *d*-camphorylideneacetate, m.p. 143°, $[\alpha] + 124.05^\circ$; *d*-, m.p. 146°, $[\alpha] + 94.21^\circ$, and *l*-hydroxymethylenecamphor *dl*-camphorylideneacetate, m.p. 146°, $[\alpha] - 91.93^\circ$. *d*-, m.p. 102°, $[\alpha] + 127.04^\circ$, *l*-, m.p. 90°, $[\alpha] + 87.58^\circ$, and *dl*-camphorylcarbinol *d*-camphorylideneacetate, m.p. 92°, $[\alpha] + 114.20^\circ$; *d*-, m.p. 90°, $[\alpha] + 19.01^\circ$, and *l*-camphorylcarbinol *dl*-camphorylideneacetate,* m.p. 91°, $[\alpha] - 23.16^\circ$. *d*-, m.p. 75°, and *dl*-camphorylacetyl chloride, an oil, b.p. 152—154°/12 mm. *d*-, an oil, $[\alpha] + 124.50^\circ$, *l*-, m.p. 111°, $[\alpha] - 55.30^\circ$, and *dl*-hydroxymethylenecamphor *d*-camphorylacetate,* m.p. 120°, $[\alpha] - 20.02^\circ$; *d*-hydroxymethylenecamphor *dl*-camphorylacetate,* m.p. 101°, $[\alpha] + 62.99^\circ$. *d*-, + MeOH, m.p. 58°, $[\alpha] + 38.76^\circ$, *l*-, $[\alpha] + 5.82^\circ$, and *dl*-camphorylcarbinol *d*-camphorylacetate, $[\alpha] + 25.74^\circ$, *d*-, $[\alpha] + 24.38^\circ$, and *l*-camphorylcarbinol *dl*-camphorylacetate, $[\alpha] - 20.92^\circ$ (four last-named esters are oils). The following properties refer to the main products of hydrogenation (Pd) of the unsaturated esters named: *d*-hydroxymethylenecamphor *d*-, m.p. 104°, $[\alpha] + 51.35^\circ$, and *dl*-camphorylpropionate, m.p. 101°, $[\alpha] + 50.01^\circ$, *d*-, m.p. 140°, $[\alpha] + 102.08^\circ$, and *dl*-camphorylideneacetate, m.p. 145°, $[\alpha] + 75.98^\circ$, and *d*-camphorylacetate, an oil, $[\alpha] + 85.44^\circ$; *l*-hydroxymethylenecamphor *d*-camphorylpropionate, m.p. 51°, $[\alpha] - 37.92^\circ$, *d*-camphorylideneacetate, an oil, $[\alpha] - 12.76^\circ$, and *d*-camphorylacetate, m.p. 74°, $[\alpha] - 22.16^\circ$; *dl*-hydroxymethylenecamphor *d*-camphorylpropionate, m.p. 102°, $[\alpha] + 47.20^\circ$, and *d*-camphorylideneacetate, m.p. 146°, $[\alpha] + 87.70^\circ$; *d*-, m.p. 150°, $[\alpha] + 75.58^\circ$, *l*-, an oil, $[\alpha] + 9.81^\circ$, and *dl*-camphorylcarbinol *d*-cam-

phorylideneacetate, m.p. 142°, $[\alpha] + 66.61^\circ$; *d*-camphorylcarbinol *dl*-camphorylideneacetate, m.p. 144°, $[\alpha] + 71.43^\circ$.
R. S. C.

Diterpenes. XXXVIII. Position of the ethylenic linking in *d*-pimaric acid. L. RUZICKA and L. STERNBACH (Helv. Chim. Acta, 1940, 23, 124—131; cf. A., 1939, II, 220).—Reactions of Me dihydro-*d*-pimarate (I) render it probable that pimarinic acid contains an ethylenic linking in position 7:8. o -CO₂H·C₆H₄·CO₂H (II) and (I) in Et₂O·CHCl₃ give an oxide (III), converted by MgMeI (which adds to the CO₂Me and partly to the O-ring) in boiling Et₂O into a mixture, which with Se at 330—345° gives pimanthrene (IV) and 1:7:8-trimethylphenanthrene (V). HCl in dry Et₂O converts (III) into Me 8-chloroisodihydro-*d*-pimarate, m.p. 122—125°, which by interaction with MgMeI (reaction with CO₂Me and partly with Cl) and subsequent Se-dehydrogenation gives (IV) and (V). Similar reactions with the dibromide of (I) give 30% of (V). Me *d*-pimarate and (II) or BzO₂H react only slowly in Et₂O, but in CHCl₃ 1.7—1.8 O are absorbed in 3 days. A solid mono-oxide is obtained, but dehydration accompanies all its transformations.
R. S. C.

Triptenes. LII. Transformation of α -boswellic acid into β -amyrin. L. RUZICKA and W. WIRZ. **LIII. Conversion of hederagenin into a transformation product of α -boswellic acid.** L. RUZICKA and A. MARXER (Helv. Chim. Acta, 1940, 23, 132—135, 144—152; cf. A., 1940, II, 18).—**LII.** Acetyl- α -boswellic acid and SOCl₂ at room temp. give the chloride, m.p. 195—196°, converted by H₂-Pd-BaSO₄ in PhMe into the aldehyde, m.p. 203—206° (vac.) after sintering (semicarbazone, m.p. 203—205°), the hydrazone, m.p. 207—209°, of which with NaOEt·EtOH at 200° gives β -amyrin. α -Boswellic acid (I) and CrO₃-AcOH at 55—60° give an α -unsaturated diketone (II), C₂₉H₄₆O₂, m.p. 222—225°, $[\alpha]_D + 7.6^\circ$ in CHCl₃ (absorption max. at 2520 Å. (log ϵ 3.1)), also obtained from nor- β -amyrin (see below).

LIII. Diacetylhederagenin and hot SOCl₂ give the acid chloride, m.p. 174°, reduced (Rosenmund) to diacetylhederaldehyde, m.p. 108—109°, the semicarbazone, m.p. 210—212°, of which with NaOEt·EtOH at 190—200° gives hederadiol, m.p. 259—261°, sublimes at 220°/0.01 mm., $[\alpha]_D + 86.8^\circ$ in CHCl₃ (dibenzoate, m.p. 186—188°, $[\alpha]_D + 128^\circ$ in CHCl₃; diacetate, an oil; CrO₃ gives a mixture), and nor- β -amyrin, C₂₉H₄₈O, m.p. 223—225°, $[\alpha]_D + 118.2^\circ$ in CHCl₃ (acetate, m.p. 198°, $[\alpha]_D + 113.5^\circ$ in CHCl₃), oxidised by CrO₃ to (II) (probably a mixture of isomerides), m.p. 218—220°, $[\alpha] + 8.0^\circ$ in CHCl₃, obtained also from (I). Interrelations of the triptenes are briefly reviewed.
R. S. C.

Triterpene group. VI. Oxidation of β -amyrin benzoate. New route to the thio-compound, C₃₀H₄₄OS. J. C. E. SIMPSON (J.C.S., 1940, 230—237).—The oxidation of β -amyrin benzoate (I) is shown to be considerably more complex than would appear from the work of Beynon *et al.* (A., 1938, II, 416) and in consequence cannot be regarded as comparable with oxidations of certain derivatives of β -boswellic acid, which give rise to single products in high yield (Simpson *et al.*, *ibid.*, 500). Hence the

criticism of Spring (Chem. and Ind., 1938, 1108) is no longer justifiable (cf. Ruzicka *et al.*, A., 1939, II, 330). The experimental conditions for oxidation of (I), which lead to pure β -amyrenonyl benzoate (II), m.p. 261.5—262.5°, $[\alpha]_D^{25} + 96^\circ$, appear to be highly crit. From the mother-liquors, there can be isolated a neutral residue, hydrolysed and acetylated to an acetate, $C_{32}H_{50}O_4$, m.p. 322—324°, $[\alpha]_D^{25} - 110^\circ$, which is hydrolysed (KOH-EtOH) to an alcohol, $C_{30}H_{48}O_3$, m.p. 284—285°; the acid fraction yields a compound, $C_{37}H_{50}O_4$, m.p. 293—294°, and a Me ester, m.p. 228—229°, $[\alpha]_D^{25} + 16.7^\circ$, in greater amount.

β -Amyranonol and BzCl in C_5H_5N give β -amyranonyl benzoate (III), m.p. 260.5—261.5°, $[\alpha]_D^{25} + 7.3^\circ$. Hydrolysis of dehydro- β -amyrenyl acetate with KOH-EtOH affords dehydro- β -amyrenol, m.p. 209—211°, which is benzoylated to the -amyrenyl benzoate (IV), m.p. 238—239°, $[\alpha]_D^{25} + 219^\circ$, and oxidised (CrO_3 -AcOH) to β -amyradienone (V), m.p. 170—171°, $[\alpha]_D^{25} + 108^\circ$ [oxime, m.p. 268.5—270° (efferv.)]. S has no action on (II) and (III) but with (IV), the thio-compound (VI), $C_{30}H_{44}OS$, obtained from β -amyrin, can be isolated. It is shown, by a comparison of the properties of (V) with those of certain compounds derived from (VI), that the chromophoric group in (VI) and its derivatives cannot consist of a system of two conjugated double linkings. All rotations are in $CHCl_3$. F. R. S.

Lignin. XXVII. Fission of ether linkings with hydrogen sulphite and thiolacetic acid. Models for the chemistry of lignin. H. RICHTZENHAHN (Ber., 1939, 72, [B], 2152—2160).— CH_2Ph guaiacyl ether is not affected by prolonged heating with $SH \cdot CH_2 \cdot CO_2H$ (I) and HCl or with aq. $NaHSO_3$ at 135°. With H_2SO_3 at 135° it affords $CH_2Ph \cdot OH$ and guaiacol (II). *p*-Nitrobenzyl guaiacyl ether, m.p. 76°, from (II), $p \cdot NO_2 \cdot C_6H_4 \cdot CH_2Cl$, and NaOMe in MeOH, is converted by aq. $NaHSO_3$ (1.4% NaOH; 4% SO_2) at 135° into $p \cdot NO_2 \cdot C_6H_4 \cdot CH_2 \cdot SO_3H$ [$\beta \cdot C_{10}H_7 \cdot NH_2$ salt, m.p. 207—208° (decomp.)], small amounts of which with much unchanged material are obtained by the action of 4% SO_2 at 135° for 48 hr. *p*-Methoxybenzyl guaiacyl ether, m.p. 97°, is little affected by (I)-HCl at 100° for 9 hr.; with aq. $NaHSO_3$ at 130° it gives Na anisylsulphonate [corresponding $\beta \cdot C_{10}H_7 \cdot NH_2$ salt, m.p. 261° (decomp.)], also obtained with H_2SO_3 . The most marked similarity with the mode of reaction of lignin is shown by phenylmethylcarbinyl guaiacyl ether, b.p. 128—130°/0.1 mm. (from *o*-OMe- $C_6H_4 \cdot ONa$ and $CHPhMeCl$ at 130°). After 24 hr. with aq. $NaHSO_3$ at 135° it is decomposed to the extent of ~33% into (II) and $CHPhMe \cdot SO_3H$ ($\beta \cdot C_{10}H_7 \cdot NH_2$ salt, m.p. 198—200°). Fission occurs also with H_2SO_3 . With (I) and HCl there is partial fission to phenylethyl- α -thiolacetic acid, identified by oxidation (KSO_4) to the corresponding sulphinacetic acid, m.p. 115—116°. With MeOH-HCl it yields phenylmethylcarbinyl Me ether, b.p. 80°/12 mm. This fission is entirely comparable with the formation of methanol-lignin. It is therefore established that those components of lignin which are not condensed to furan or pyran rings suffer fission with $NaHSO_3$, (I), or HCl-MeOH as previously assumed. *o*-

OMe- $C_6H_4 \cdot ONa$ in C_6H_6 and cinnamyl bromide at 100° yield cinnamylguaiacol, m.p. 51—52° (acetate, m.p. 88°), with guaiacyl cinnamyl ether, m.p. 76—77°; the former is cyclised by prolonged boiling with anhyd. HCO_2H into 8-methoxyflavan (III), m.p. 130—132°. Attempted fission with (I) leaves flavan and (III) untouched whilst partial resinification unaccompanied by production of sulphonic acids is caused by $NaHSO_3$ or SO_2 . Examination of flavanone shows that the presence of CO in a ring containing O facilitates fission since $NaHSO_3$ or SO_2 gives β -*o*-hydroxybenzoyl- α -phenylethyl- α -sulphonic acid [*Na*, *Ba*, *Pb*, and $\beta \cdot C_{10}H_7 \cdot NH_2$, m.p. 191—192° (decomp.), salts], which couples with diazonium salts. Fission does not take place with (I). H. W.

Celastrol. II. O. GISVOLD (J. Amer. Pharm. Assoc., 1940, 29, 12—14; cf. A., 1939, II, 484).—Re-examination of celastrol gives the formula $C_{22}H_{30}O_3$. One OH can be methylated by CH_2N_2 and the two remaining O appear to be present as an *o*-quinone.

F. O. H.

Isomerisation of zeaxanthin and physalien. L. ZECHMEISTER, L. VON CHOLNOKY and A. POLGAR (Ber., 1939, 72, [B], 1678—1685).—Zeaxanthin, obtained from the berries of *Lycium halimifolium*, has m.p. 205° (block), $[\alpha]_D - 40^\circ$ to -42.5° in $CHCl_3$. If its freshly prepared solution in C_6H_6 is boiled for 30 min. under a reflux condenser or kept at room temp. with I for 30 min. $[\alpha]_D$ becomes positive owing to the formation of neozeaxanthin A, m.p. ~106° (corr.), $[\alpha]_D + 113^\circ$ in $CHCl_3$. Neozeaxanthin B appears sometimes dextro- and sometimes laevorotatory but the small val. of α_D does not permit certain measurement. Neozeaxanthins A and B are so closely similar that they can only be distinguished in solution by the polarimeter; the spectroscopy is useless. Their difference from natural zeaxanthin is established by marked spectroscopic and chromatographic differences; the latter are not observable in an Al_2O_3 column, which has a too powerful action. Dextrorotatory zeaxanthin preps. have never been observed but it is not yet possible to bring it finally into the steric series of the polyene alcohols. Physalien has $[\alpha]_D - 45^\circ$ in $CHCl_3$, -31° in C_6H_6 . It is readily reversibly isomerised, thereby producing a single pigment, neophysalien, $[\alpha]_D - 21^\circ$ to -22° in $CHCl_3$, which could not be caused to crystallise. In the chromatogram it lies immediately below the natural material. It appears that the process of isomerisation can be elucidated only by physical methods. All carotenoids which have been investigated give isomerides of greater solubility, lower m.p., and more pronounced absorption in the region of shorter λ . In the column the epiphasic (or partly hypophasic) free polyenes, β - and α -carotene, lycopene, cryptoxanthin, physalien, natural and synthetic capsanthin and capsorubin dipalmitate, and carotene give isomerides which are somewhat more feebly adsorbed than the natural product. The pronouncedly hypophasic carotenoids with at least two free OH [zeaxanthin, lutein (xanthophyll), taraxanthin, capsanthin, and capsorubin] are converted into pigments with much superior adsorptive power. All the phenomena do not appear explicable by the

migration of double linkings and the assumption of *cis-trans*-isomerisation seems more promising.

H. W.

Influence of acyl group in position 3 on reactions of chromones. II. Action of aluminium chloride on 7-benzoyloxy-3-acetyl-2-methylchromone. G. R. KELKAR and D. B. LIMAYE (Rasāyanam, 1939, 1, 183—185; cf. A., 1936, 854; 1937, II, 254).—7-Benzoyloxy-3-acetyl-2-methylchromone, m.p. 167°, and AlCl_3 at 160—170° give 7-hydroxy-3-acetyl-2-methylchromone (Ac inhibits Fries migration). 7-Benzoyloxy-2-methylchromone, m.p. 125°, is transformed by AlCl_3 into 7-hydroxy-8(6)-benzoyl-2-methylchromone, m.p. 205°. 7-Acetoxy- or 7-benzoyloxy-2:3-dimethylchromone, m.p. 146°, and AlCl_3 afford 7-hydroxy-8-acetyl-, m.p. 215° (7-OMe-derivative, m.p. 130°) (converted by N-NaOH into 2:4-dihydroxy-3-acetylbenzoic acid), or -benzoyl-2:3-dimethylchromone, m.p. 208°, respectively.

A. T. P.

Monohydroxycoumarins. H. BÖHME (Ber., 1939, 72, [B], 2130—2133).—8-Methoxycoumarin is demethylated by AlBr_3 in boiling C_6H_6 to 8-hydroxycoumarin, m.p. 160° , from which it is re-formed by CH_2N_2 in Et_2O . 8-Acetylcoumarin has m.p. 131° . 2:6:1-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$, NaOAc , and Ac_2O at 150 — 160° and subsequently at 175 — 180° afford 5-acetylcoumarin, m.p. 84° , hydrolysed by boiling 25% H_2SO_4 to 5-hydroxycoumarin, m.p. 229° (*Me ether*, m.p. 75 — 77° after softening at 70°). H. W.

H. W.

Synthesis in the furocoumarin group. Angular and linear furocoumarins. VI. D. B. LIMAYE, R. H. MUNJE, G. S. SHENOLIKAR, and S. S. TATWALKAR. VII. V. K. BHAGWAT and R. Y. SHAHANE (Rasāyanam, 1939, 1, 187—189, 190; cf. A., 1937, II, 258).—VI, VII. The following are described: 8-*acetyl*-, m.p. 200° (*Et* ester, m.p. 108°); 6-, m.p. 241° (*Et* ester, m.p. 163°), and 8-*propionyl*-, m.p. 208° (*Et* ester, m.p. 85°); o-, m.p. 206° (*Et* ester, m.p. 145°), m-, m.p. 190° (*Et* ester, m.p. 128°), and p-*toluoyl*-, m.p. 188° (*Et* ester, m.p. 130°); 6-, m.p. 222—224° (*Et* ester, m.p. 164°), and 8-n-*butyryl*-, m.p. 160° (*Et* ester, m.p. 86°); 6-, m.p. 203° (*Et* ester, m.p. 149°), and 8-n-*valeryl*-7-*carboxymethoxy*-4-*methylcoumarin*, m.p. 136° (*Et* ester); 8-*benzoyl*-7-*carboxymethoxy*-4-*phenylcoumarin*, m.p. 203° (*Et* ester, m.p. 122°). Derived from these are: 4'-*phenyl*-3-*methyl*-, m.p. 153°, 3-*ethyl*-4'-*methyl*-, m.p. 137°, 3-o-, m.p. 165°, -m-, m.p. 190°, and -p-*tolyl*-4'-*methyl*-, m.p. 175°, 3-n-*propyl*-, m.p. 85°, and -*butyl*-4'-*methyl*-, m.p. 89°, and 3:4'-*diphenyl*-7':8'-*furocoumarin*, m.p. 154°; 3-*ethyl*-, m.p. 177°, -n-*propyl*-, m.p. 175°, and -*butyl*-4'-*methyl*-6':7'-*furocoumarin*, m.p. 158°.

A. T. P.

Synthesis in the coumarin- γ -pyrone group.
 III. Synthesis of 4 : 2'-dimethyl-8-ethyl-6 : 7- γ and 4 : 4'-dimethyl-8-ethyl-6 : 7- α -pyronocoumarin. D. B. LIMAYE and (MISS) I. GHATE (Rasāyanam, 1939, 1, 169—176; cf. A., 1938, II, 250).—2-Ethylresorcinol and $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et} \cdot \text{H}_2\text{SO}_4$ give 4-methyl-8-ethylumbelliferone (I), m.p. 224° [acetate (II), m.p. 104° ; benzoate, m.p. $147\text{--}149^\circ$]; its *Me* ether, m.p. 133° , and x-NaOH give 2-hydroxy-4-methoxy-3-ethyl- β -methylcinnamic acid, m.p. $104\text{--}105^\circ$

(decomp.), reconverted readily into the above ether. (II) and AlCl_3 at $160\text{--}165^\circ$ afford 6-*acetyl-4-methyl-8-ethylumbelliferone* (III), m.p. 166° (semicarbazone, m.p. $>270^\circ$; acetate, m.p. 105°), hydrolysed by N-NaOH to 5-*acetyl-2:4-dihydroxy-3-ethyl- β -methylcinnamic acid* (IV), m.p. 133° (decomp.) [H_2SO_4 gives (III)], and β -(5'-*acetyl-2':4'-dihydroxy-3'-ethylphenyl*)-*propylene*, m.p. 70° [also by heating (IV) at $>\text{m.p.}$]. (III) and $\text{NaOAc-Ac}_2\text{O}$ at $160\text{--}170^\circ$ give 3'-*acetyl-4:2'-dimethyl-8-ethyl-6:7- γ -* (V), m.p. 225° (no CHPh: derivative is formed), and 4:4'-*dimethyl-8-ethyl-6:7- α -pyronocoumarin* (VI), m.p. 285° . (V) and N-NaOH give 4-*methyl-8-ethylumbelliferone-6-carboxylic acid* (VII), m.p. 275° (decomp.) [decarboxylated to (I)], 4:2'-*dimethyl-8-ethyl-6:7- γ -pyronocoumarin*, m.p. 208° (VIII) (CHPh: derivative, m.p. $174\text{--}175^\circ$) [also from (IX) and H_2SO_4], and β -6-(7-*hydroxy-2-methyl-8-ethylbenzo- γ -pyrro*no)- β -*methylacrylic acid* (IX), m.p. 205° (decomp.) ($+\text{H}_2\text{O}$ or anhyd.) [also from (VIII) and NaOH]. (IX) is hydrolysed to (IV). (IX) at 210° gives β -6-(7-*hydroxy-2-methyl-8-ethylbenzo- γ -pyrro*no)propylene, m.p. $144\text{--}146^\circ$ (*Me ether*, m.p. 110°). (VI) and N-NaOH give β -6-(7-*hydroxy-4-methyl-8-ethylbenzo- α -pyrro*no)- β -*methylacrylic acid*, m.p. 171° [gives (VI) with H_2SO_4], 2-ethylresorcinol, and a compound, m.p. $220\text{--}225^\circ$. (VII) and aq. NaOH give a substance, m.p. 130° (decomp.), then solidified and m.p. 235° (decomp.), decarboxylated to β -(2:4-*dihydroxy-3-ethyl-5-carboxyphenyl*)propylene, m.p. $241\text{--}242^\circ$ (decomp.). A. T. P.

A. T. P.

Natural coumarins. L. Constitution of nodakenin from *Peucedanum decursivum*, Maxim. E. SPÄTH and E. TYRAY (Ber., 1939, 72, [B], 2089—2092; cf. Arima, A., 1927, 599; Späth and Kainrath, A., 1936, 1387).—Cautious oxidation of nodakenetin (I) yields COMe₂, thus establishing the constitution

$$\begin{array}{c} \text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}:\text{CH}_2 \\ \text{CO}-\text{O}-\text{CH}:\text{CH}:\text{CH}-\text{O} \end{array} > \text{CH} \cdot \text{CMe}_2 \cdot \text{OH}. \quad \text{Nodakenin}$$

tetra-acetate (II) has m.p. 195—196°. (I) does not react with acetobromoglucose in Et₂O containing Ag₂CO₃ or in org. bases. (I), β-*D*-glucose pentaacetate, and a trace of *p*-C₆H₄Me·SO₃H at 125—130° yield a small amount of (II), hydrolysed to nodakenin, m.p. 221.5—222° (vac.), [α]_D²⁰ +57.7° in H₂O.

H. W.

Natural coumarins. II. Synthesis of xanthyletin. E. SPÄTH and R. HILLEL (Ber., 1939, 72, [B], 2093—2094).—Repetition of previous work (A., 1939, II, 335) by an improved method shows that xanthyletin is formed in minor amount (with seselin) by the action of umbelliferone on β -methyl- Δ^7 -butin- β -ol.

H. W.

Constitution of rottlerin. J. N. RAY, K. S. NARANG, and B. S. ROY (Current Sci., 1939, 8, 558).—Rottlerin Me ether (A., 1938, II, 66) has $\alpha + 5.75^\circ$ (2% in CHCl_3). An *as*-C atom is not present in the formula of McGookin *et al.* (A., 1939, II, 559). It is maintained, in opposition to these authors, that an acidic substance is formed in the conversion of tetrahydrottlerin into octahydrottlerone. W. O. K.

Valency angle studies. V. Stereochemistry of the sulphone group. A. LÜTTRINGHAUS and K. BUCHHOLZ (Ber., 1939, 72, [B], 2057—2062; cf. A., 1939, 1, 337).—X-Ray observations have assigned the

val. $112.4 \pm 1.5^\circ$ to the angle at the S atom of the strain-free ether $S < \begin{smallmatrix} C_6H_4 \cdot O \\ C_6H_4 \cdot O \end{smallmatrix} > [CH_2]_{10}$ and therefrom comparative ring-closure experiments show the angle $110 \pm 3^\circ$ for CH_2 in $CH_2(C_6H_4 \cdot OH)_2$. A similar comparative determination from the yield curves is impossible for SO_2 by reason of the differing rate of etherification of OH in the sulphone. It is here necessary to estimate the angle from the minimal bridge length necessary for successful ring-closure. Since success is reached with $(CH_2)_5$ the angle at SO_2 is deduced geometrically to be $\sim 75^\circ$. The tetrahedral arrangement of the four substituents of SO_2 is therefore greatly distorted. The validity of the calculation is discussed and the highest possible val. is considered to be 90° . Gradual addition of 3.32N-KOH-EtOH to a boiling solution of $Br \cdot [CH_2]_{10} \cdot Br$ and $SO_2(C_6H_4 \cdot OH-p)_2$ in EtOH affords 4:4'-dihydroxydiphenyl sulphone κ -bromodecyl ether (I), which is non-cryst. and cannot be distilled without decomp.; it is purified by treatment with Claisen alkali. The ζ -bromohexyl, ϵ -bromoamyl, and γ -bromopropyl (II) ethers are obtained analogously. Gradual addition of (I) in amyl alcohol to a boiling suspension of K_2CO_3 in the same solvent leads to 4:4'-dihydroxydiphenyl sulphone decamethylene ether, $SO_2 < \begin{smallmatrix} C_6H_4 \cdot O \\ C_6H_4 \cdot O \end{smallmatrix} > [CH_2]_{10}$, m.p. 144.5° , in 24.4% yield. Analogously obtained are the hexamethylene ether, m.p. 155° (yield 10%), and pentamethylene ether, m.p. 202° (yield 5.7%). Similar experiments with (II) give polymerised products and no evidence of intramol. ring-closure.

H. W.

Production of glutamine by amination of pyrrolidonecarboxylic acid. N. LICHTENSTEIN (Enzymologia, 1939, 7, 383).—Pyrrolidonecarboxylic acid (5 g.), obtained by heating glutamic acid for ~ 30 min. at 180 – 185° , yields 0.4 g. of glutamine when left for 4 days in 10 parts of 25% aq. NH_3 .

W. McC.

Pyrrolines. A. SONN [with E. NEUMANN and E. BREHMER] (Ber., 1939, 72, [B], 2150–2151).—Reduction of Ph γ -nitroisobutyl ketone (obtained by the condensation of crotonyl bromide and $MeNO_2$) with Fe powder in AcOH yields 2-phenyl-4-methyl- Δ^2 -pyrroline, b.p. $124^\circ/12$ mm. (picrate, m.p. 192°), also obtained by the action of Zn dust and HCl on 2-phenyl-4-methylpyrrole.

H. W.

Synthesis of 1-methyl-2:6-di(dicarbethoxymethylene)piperidine. Y. F. CHI, C. C. KUAN, C. LIU, and G. C. LU (J. Chem. Eng. China, 1938, 5, 65–66).— $Et_2\beta\zeta$ -diketo- $\alpha\eta$ -dicarbethoxyazolate with NH_2Me in EtOH at 140 – 150° yields 1-methyl-2:6-di(dicarbethoxymethylene)piperidine, b.p. 139 – $142^\circ/1$ mm., and a N-free compound, b.p. 82 – $85^\circ/1$ mm.

F. R. G.

Complex compounds of platinum and complex amines.—See A., 1940, I, 172.

Deutero-2-pyridone.—See A., 1940, III, 237.

Separation of β -picoline, γ -picoline, and 2:6-lutidine from their mixture. A. G. LIDSTONE (J.C.S., 1940, 241–243).—The bases are converted into oxalates and these are crystallised from EtOH. γ -Picoline oxalate, m.p. 137 – 138° , is readily obtained

(base:acid, 4:5); β -picoline oxalate, m.p. 119 – 121° , separates somewhat less readily (base:acid, 2:3). 2:6-Lutidine remains in the original mother-liquor and is separated as the mercurichloride from dil. HCl.

F. R. S.

Nicotinic acid and its amide. V. H. MIKKELSEN (Arch. Pharm. Chemi, 1939, No. 18, 20 pp.).—Published preps. of nicotinamide (I) are reviewed and improvements in detail given. (I) has m.p. 130 – 132° (corr.), lower vals. being due to the presence of nicotinic acid (up to 4% in commercial preps.), which can be removed by treating the solution in $COMe_2$ with Ca silicate. The solubilities of (I) in H_2O , EtOH, Et_2O , glycerol, $COMe_2$, and C_6H_6 have been determined. (I) is readily hydrolysed by 2N- but not by 0.1N-HCl or 0.001N-NaOH at 120° and solutions may thus be sterilised safely. (I) has $K_A = 10^{-12.9}$ and $K_B = 10^{-10.9}$.

M. H. M. A.

Pyridine sulphonamides.—See B., 1940, 244.

Synthesis of adermin. S. MORII and K. MAKINO (Enzymologia, 1939, 7, 385–386; cf. Kuhn *et al.*, A., 1939, II, 487).— $OMe \cdot CH_2 \cdot CO_2Et$ and $COMe_2$ in presence of Na give $OMe \cdot CH_2 \cdot CO \cdot CH_2 \cdot COMe$, which with $CN \cdot CH_2 \cdot CO \cdot NH_2$ in presence of piperidine yields 2-hydroxy-3-cyano-6-methyl-4-methoxymethylpyridine, m.p. 226° . This, with HNO_3 in Ac_2O , yields the corresponding 5- NO_2 -compound, m.p. 210° , which with PCl_5 in PhCl gives 2-chloro-5-nitro-3-cyano-6-methyl-4-methoxymethylpyridine (I), m.p. 70 – 73° . (I) with H_2 -PtO₂ or H_2 -Pd-C gives the hydrochloride of 5-amino-6-methyl-3-aminomethyl-4-methoxymethylpyridine, m.p. 147° , which is converted by $NaNO_2$ into adermin 4-Me ether. The 4-Et ether, m.p. 134° , is obtained by way of 2-hydroxy-, m.p. 210° , 5-nitro-2-hydroxy-, m.p. 157° , 2-chloro-5-nitro-, m.p. 45° , and 2-chloro-5-amino-, m.p. 146° , -3-cyano-6-methyl-4-ethoxymethylpyridine, and the hydrochloride, m.p. 126° , of 5-amino-6-methyl-3-aminomethyl-4-ethoxymethylpyridine (picrate, m.p. 188°). No preparative details are given.

W. McC.

isoQuinoline series. IV. Syntheses of benzoisoquinolones. Preparation of isoquinolines from naphthalene derivatives. B. B. DEY and S. RAJAGOPALAN (Arch. Pharm., 1939, 277, 359–374; cf. A., 1939, II, 388).—2:1- $OMe \cdot C_{10}H_6 \cdot CH \cdot N \cdot OH$ and 4.5% Na-Hg in EtOH give β - $C_{10}H_7 \cdot OMe$ and 2-methoxy-1-naphthylmethylamine, $NH_2 \cdot CH_2Ar$, sinters at 40° , m.p. 41 – 42° [Ac (I), m.p. 172° , and Bz derivative, m.p. 155° ; picrate, m.p. 215° (decomp.)]. β - $C_{10}H_7 \cdot OH$ and $(CH_2)_6N_4$ in AcOH at 100° give 2:1- $OH \cdot C_{10}H_6 \cdot CHO$ and 2-hydroxy-1-naphthylmethylamine, $NH_2 \cdot CH_2Ar$, m.p. 135 – 138° [N-Ac, m.p. 160° [Me ether = (I)], ON-Ac, m.p. 171 – 172° , and -Bz₂ derivative, m.p. 212°]. Prep. of 4-keto-7-methoxy-1-phenyl-3:4-dihydro-5:6-benzoisoquinoline from 1:4- $OMe \cdot C_{10}H_6 \cdot CO \cdot CH_2 \cdot NHBz$, and of 4-keto-1-methyl-3:4-dihydro-5:6- and -7:8-benzoisoquinoline from α - and β - $C_{10}H_7 \cdot CO \cdot CH_2 \cdot NHAc$, respectively, by $POCl_3$ in xylene is announced without details. Known methods of preparing benzoisoquinolines are reviewed. Other methods failed.

R. S. C.

Nitrogen ring derivatives of anthraquinone etc.—See B., 1940, 119, 120.

5-Alkyl-5- α -sec.-butoxyethylhydantoins. R. J. SPEER and H. R. HENZE (J. Amer. Chem. Soc., 1939, 61, 3376—3377).—COR·CHMe·O·CHMeEt, KCN, and $(\text{NH}_4)_2\text{CO}_3$ in 50% EtOH at 55—60° give 22—41% of 5-methyl-, m.p. 203—204°, 5-ethyl-, m.p. 190°, 5-n-, m.p. 205—206°, and 5-iso-propyl-, m.p. 196—197°, 5-n-, m.p. 204—205°, 5-iso-, m.p. 192°, and 5-sec.-butyl-, m.p. 189—190°, 5-n-, m.p. 178°, and 5-iso-amyl-, m.p. 177°, 5- α -sec.-butoxyethylhydantoin. M.p. are corr. R. S. C.

Pyridine and piperazine derivatives of sulph-anilamide. W. O. KERMAK and W. TEBRICH (J.C.S., 1940, 202—206).—2-Aminopyridine and 3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NHAc})\cdot\text{SO}_2\text{Cl}$ in dry $\text{C}_5\text{H}_5\text{N}$ give 2-(3'-nitro-4'-acetamidobenzenesulphonamido)pyridine, m.p. 270°, hydrolysed to the 4'- NH_2 -compound, m.p. 232°, which with NaOH forms the 4'-OH-derivative, m.p. 234°; this compound is reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to the 2-(3'- NH_2 -derivative, m.p. 211°. Piperazine and p-NHAc· $\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ (I) afford 1:4-di-(p-acetamidobenzenesulphonyl)piperazine, m.p. 324°, hydrolysed (KOH) to the p- NH_2 -compound, m.p. 331—332°. Et piperazine-1-carboxylate and (I) yield Et 4-(p-acetamidobenzenesulphonyl)piperazine-1-carboxylate, m.p. 132°, hydrolysed (KOH) to the p- NH_2 -compound (II), m.p. 170°, and further hydrolysed (KOH) to 1-p-aminobenzenesulphonylpiperazine, m.p. 204°. In dry $\text{C}_5\text{H}_5\text{N}$ (I) and (II) give Et 4-(p-acetamidobenzenesulphonamidobenzenesulphonyl)piperazine-1-carboxylate, m.p. 194°. F. R. S.

1-Phenyl-3-methyl-4-acetylvinyl-5-pyrazolone and 5-acetylvinyl-2-thio-2:4:6-triketohexahydropyrimidine.—See B., 1940, 194.

Pyrimidines. Molecular rearrangement of 2:6-dimethoxy-4-methyl-5-n-propylpyrimidine. Y. F. CHI, S. S. WEI, and M. S. LIANG (J. Amer. Chem. Soc., 1939, 61, 3377—3379).—4-Methyl-5-n-propylthiouracil in $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ gives 4-methyl-5-n-propyluracil (I), m.p. 246—247°, which with POCl_3 at 120—130° gives 2:6-dichloro-4-methyl-5-n-propylpyrimidine, m.p. 31—33°, b.p. 149°/20.8 mm., converted by NaOMe-MeOH into 2:6-dimethoxy-4-methyl-5-n-propylpyrimidine (II), b.p. 135—140°/19.5 mm. With NaOEt-Me₂SO₄-EtOH or Me₂SO₄-aq. NaOH, (I) gives 1:4-dimethyl-5-n-propyluracil, m.p. 193.5—194°. At 260—280° (II) gives 1:3:4-trimethyl-5-n-propyluracil, m.p. 74—75°, but with MeI at 50—60° rearrangement stops half-way, yielding 2-keto-6-methoxy-3:4-dimethyl-5-n-propylpyrimidine (III), cryst., b.p. 180—182°/4.5 mm., hydrolysed by hot, dil. HCl to 3:4-dimethyl-5-n-propyluracil, m.p. 148—150°, also obtained from (III) at 330—350°. 2:6-Diethoxy-4-methyl-5-n-propylpyrimidine, b.p. 145—148°/18 mm., is prepared. R. S. C.

1:1'-Dithiol-3:3'-bisisoindolenylidene.—See B., 1940, 192.

Reduction of 1:2:3-benzotriazole and its methyl derivatives by sodium in liquid ammonia. N. O. CAPPEL and W. C. FERNELIUS (J. Org. Chem., 1940, 5, 40—47).—1:2:3-Benzotriazole (I) and Na in liquid NH_3 form equimol. amounts of

the Na salts (II) of (I) and its H_2 -derivative (III). Active H ($\text{NH}_4^+ + e^-$) reduces the former but not the latter salts to o- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ (IV) [Bz_2 derivative, m.p. 152.8—153.8°; $(\text{SO}_2\text{Ph})_2$ compound, m.p. 156—157°]. A solution of Na in liquid NH_3 does not react with 1- (V) or 2- (VI) -methylbenzotriazole, with (II), or with (III). Active H ($\text{NH}_4^+ + e^-$) reduces (VI) to (IV) and (V) to o- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$. H_2 generated by the action of K on liquid NH_3 in presence of Fe is relatively ineffective in reducing the K derivative of (I) to (IV). It has been shown previously that organo-metallic compounds are first formed in liquid NH_3 and are solvolysed, giving rise to the hydrogenated product. It is now evident that active H may also play an important rôle and that the effects of the two mechanisms may be separately evaluated, at least for the benzotriazoles. The question is one of relative ease of addition of electrons and of H atoms. The triazole nucleus is stable towards electrons but is broken down by H atoms. If it is required to obtain only the reduction product due to the electron and not to active H and an initial excess of Na is desirable for the sake of rapidity and completeness, the excess of metal may be destroyed by NaNO_3 (probable reaction, $\text{NaNO}_3 + 3\text{Na} + \text{NH}_3 \rightarrow \text{Na}_2\text{NO}_2 + \text{NaOH} + \text{NaNO}_2$) provided that the Na_2NO_2 is decomposed by NH_4 salts before evaporation of NH_3 . Complications due to the use of H_2O , NH_4 salts, or ammonolysis catalysts are thus avoided.

H. W.

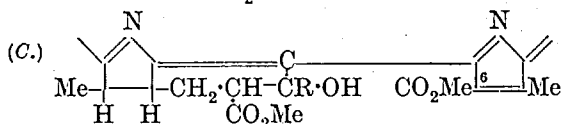
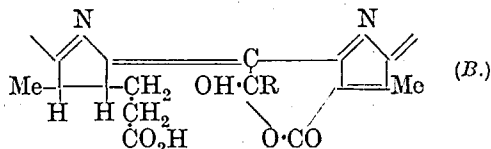
Induced oxidation in the autoxidation of xanthine.—See A., 1940, I, 168.

Chlorophyll. LXXXIX. Vinyl-, hydroxy-ethyl-, and oxo-phyllporphyrin. H. FISCHER and S. F. MACDONALD. XC. 2- α -Hydroxymeso-isochlorin e_4 dimethyl ester and vinylisochloroporphyrin e_4 . H. FISCHER and J. M. ORTIZ-VELEZ. XCI. iso- and neo-purpurins. H. FISCHER and M. STRELL (Annalen, 1939, 540, 211—223, 224—232, 232—249).—LXXXIX. Short treatment of chlorin e (I) with boiling quinoline in N_2 gives phyllochlorin (II) [identical with the pyrochlorin e of Conant *et al.* (A., 1931, 368)], vinylphyllporphyrin [1:3:5:8: γ -pentamethyl-4-ethyl-7- β -carboxyethyl-2-vinylporphyrin] (III) (Me ester, m.p. 238°), and phylloporphyrin (IV); Conant's method of decarboxylation affords (II) and (III). Chloroporphyrin e_3 (A., 1930, 482) [from (I) and boiling HCO_2H] and pyrochloroporphyrin (Conant) are mixtures of (III) and (IV). Reduction (H_2 , Pd, COMe_2) of (III) gives (IV). Conversion of $\cdot\text{CH}\cdot\text{CH}_2$ into $\cdot\text{COMe}$ occurs when (II) (also undergoes dehydrogenation at $\text{C}_{(7)}$ and $\text{C}_{(9)}$) or (III) (as Me esters) are treated with air in AcOH-HI for 2—3 weeks; subsequent treatment with CH_2N_2 affords oxophyllporphyrin Me ester (V), m.p. 257° (272° after Kofler-Hilbck) [Cu salt, m.p. 278° (corr.); oxime, m.p. 290° (corr.; decomp.)], reduced (boiling conc. EtOH-KOH; followed by CH_2N_2) to 2- α -hydroxyethyl-2-de-ethylphyllporphyrin Me ester (VI), m.p. 209—210°, which is oxidised (KMnO_4 , $\text{C}_5\text{H}_5\text{N}$) to (V). When a solution of (VI) in AcOH is evaporated to dryness and the residue kept at 100° (bath) for several hr. some (III) is produced; AcOH-HBr (1 week) followed by aq. NaOAc converts (III)

(as ester) into (VI). The change (VI) \rightarrow (V) can also be effected with AcOH-HI.

XC. *iso*Chlorin e_4 Me₂ ester (I) (*hæmin*) (cf. A., 1935, 1382) adds HBr (in AcOH) to the $\cdot\text{CH}\cdot\text{CH}_2$; subsequent hydrolysis (15% HCl at room temp.) and esterification (CH_2N_2) gives 2- α -hydroxymesoisochlorin e_4 Me₂ ester, m.p. 170° [at 180°/10 min. in a high vac. affords (I)], oxidised (KMnO_4 , $\text{C}_5\text{H}_5\text{N}$) to 2-acetyl-*isochlorin* Me₂ ester, m.p. 243°. *Vinylisochloroporphyrin* e_4 Me₂ ester, m.p. 224° (*hæmin*, m.p. 278°; *Cu* salt, m.p. 221°), is obtained from (I) and Fe powder in 80% HCO_2H at $\sim 100^\circ$. A little pyrophosphoribide *a* results from *isochlorin* e_4 and P_2O_5 + sand at 100° (bath). *Mesoisochlorin* e_4 Me₂ ester (*hæmin*, m.p. 223°; *Cu* salt, m.p. 125°) and Br-AcOH- CHCl_3 followed by COMe_2 give a compound, $\text{C}_{35}\text{H}_{41}\text{O}_4\text{N}_4\text{Br}_2$, m.p. 171° (*Cu* salt, m.p. 133°).

XCI. Dihydroxychlorin e_6 (cf. A., 1937, II, 470) with O_2 in boiling $\text{C}_5\text{H}_5\text{N}$ gives the non-cryst. dihydroxypurpurin 5 (I) and *dihydroxy- γ -hydroxymethyl-rhodochlorin lactone*, m.p. 180° (cf. *loc. cit.*). Application of the neopurpurin reaction (A) (A., 1939, II, 288) [short treatment with cold PrOH-KOH in $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ followed by re-esterification (CH_2N_2)] to (I) (as Me₂ ester) affords the dextrorotatory *dihydroxyneopurpurin* 4, m.p. 191°. Neopurpurin 4 Me₂ ester (II) (*Cu* salt, m.p. 245°) is reduced (H_2 , Pd, dioxan) to *mesoneopurpurin* 4 Me₂ ester, m.p. 202°, also obtained (A) from mesopurpurin 5 Me₂ ester. Purpurin 5 Me₂ ester (III) in $\text{C}_5\text{H}_5\text{N}$ with $\text{MeOH}-\text{Ba}(\text{OH})_2$ gives the unstable *chlorin* 5, $\text{C}_{33}\text{H}_{34}\text{O}_5\text{N}_4$ (IV)



(B, R = H), m.p. $>300^\circ$ (cf. A., 1939, II, 287), which with $\text{Et}_2\text{O}-\text{CH}_2\text{N}_2$ affords (III) and with AcOH-HI yields chloroporphyrin e_5 lactone (V); (IV) does not give (A). Short treatment (1 min.) of (III) with cold 5% MeOH-KOH gives *isopurpurin* 5 Me₂ ester (VI) (C, R = H), m.p. 210°, converted by warm MeOH-KOH into (II) (free acid) and (IV), by AcOH-HI into (V), and unaffected by O_2 in $\text{C}_5\text{H}_5\text{N}$; (VI) is considered to be an intermediate in the prep. (A) of (II) from (III). Successive treatment of (VI) with boiling 20% MeOH-KOH (1–2 min.) and CH_2N_2 affords 2-vinylchloroporphyrin e_5 Me ester, m.p. $>300^\circ$, and 2-vinylrhodoporphyrin, whilst reduction (H_2 , Pd, dioxan) gives *mesoisopurpurin* 5 Me₂ ester, m.p. 183°. Dihydroxyisopurpurin 5 is obtained [as for (VI)] from (I) (Me₂ ester), whilst purpurin 7 Me₃ ester similarly affords (after esterification) *isopurpurin* 7 Me₃ ester (C, R = CO_2Me), m.p. 270°, converted (A) into an unstable *chlorin* 7 (B, R = CO_2H) and by AcOH-HI into *phaeoporphyrin* a_7 Me₂ ester. The OH of (B) or (C) could not be acetylated or benzoylated. 10-Acetoxymethylphosphoribide *a* undergoes methanolysis with anhyd. Na_2CO_3 in $\text{MeOH}-\text{C}_5\text{H}_5\text{N}$ to

(probably) rhodochlorin Me ester; with $\text{MeOH}-\text{CH}_2\text{N}_2$ some chlorin e_7 lactone may be formed.

H. B.

Structural interpretation of the acidity of groups associated with the hæms of hæmoglobin and derivatives.—See A., 1940, III, 343.

Phthalocyanine sulphochloride.—See B., 1940, 122.

Formation of "skatole-red" from normal human urine.—See A., 1940, III, 224.

*iso*Oxazole group. VIII. Sulphonic derivatives. IX. *iso*Oxazolesulphonic acids. A. QUILICO and R. JUSTONI (Gazzetta, 1940, 70, 3–11, 11–18).—VIII. 5- (I) (87%) and 3-methyl-*iso*-oxazole (II) (13%) with ClSO_3H at 100° for 24 hr. give some 5-methylisooxazole-4-sulphonyl chloride (III), m.p. 23°, stable to cold H_2O , and, after treatment with PbCO_3 , (III) and the *Pb* salt of the -4-sulphonic acid [*Na* (IV), *Ca*, and *Ba* salts; *anilide* (V), m.p. 64°]. (II) is recovered unchanged, but with ClSO_3H at 120–125° gives 3-methylisooxazole-4-sulphonyl chloride, an oil, stable to H_2O , and the -4-sulphonic acid [*Na* salt (+2 H_2O) (VI); *Ca* and *Pb* salts; *anilide*, m.p. 62.5°]. Reference is made to products from 3:5-dimethylisooxazole (VII) (see below).

IX. With 30% NaOH , (IV) gives NH_3 and $\text{Na}_2\alpha$ -sulphonylacetate (+ H_2O), hydrolysed by 20% HCl and BaCl_2 to BaSO_4 , CO_2 , and COMe_2 . With 10% KOH , followed by diazotised $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, (V) gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CHAc}\cdot\text{CN}$. When boiled with excess of NH_2Ph , (III) gives β -*anilo- α* -(*anilido-sulphonyl*)-*n*-butyronitrile, m.p. 159–160°. With 30% NaOH , (VI) gives $\text{SO}_3\text{Na}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, NaOAc , and NH_3 . (VII) is sulphonated to 3:5-dimethylisooxazole-4-sulphonyl chloride, m.p. 34°, and to the -4-sulphonic acid, m.p. $\sim 50^\circ$ [*Na* salt (+ H_2O); *amide*, m.p. 166–167°; *anilide*, m.p. 122°].

E. W. W.

Chalkones: production of *isooxazoles* from some chalkone derivatives. R. B. SHENOI, R. C. SHAH, and T. S. WHEELER (J.C.S., 1940, 247–251).—The action of NH_2OH in presence of alkali on a chalkone dibromide $\text{R}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{R}'$ provides an unambiguous synthesis of the resulting *isooxazole*, $\text{CR}\leq\text{CH}\cdot\text{CR}'$ (I), and the reaction can therefore be employed to determine which of the two possible *isooxazoles*, (I) or $\text{CR}\leq\text{CH}\cdot\text{CR}'$ (II), is obtained from the related dibenzoylmethane, $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}'$ (III), and NH_2OH . No simple relation can be traced between the substituents in (III) and the structure of the preferred *isooxazole*. Examples of (III) which give type (I): R = $p\text{-C}_6\text{H}_4\cdot\text{OMe}$, R' = Ph; R = Ph, R' = 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}$ (6); R = $p\text{-C}_6\text{H}_4\text{Me}$, R' = Ph; R = $p\text{-C}_6\text{H}_4\text{Me}$, R' = $p\text{-C}_6\text{H}_4\cdot\text{OMe}$; R = $o\text{-C}_6\text{H}_4\cdot\text{OH}$, R' = Ph; R = Ph, R' = 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$; R = $p\text{-C}_6\text{H}_4\text{Cl}$, R' = 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$; R = $p\text{-C}_6\text{H}_4\text{Me}$, R' = 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$; R = $p\text{-C}_6\text{H}_4\text{Me}$, R' = 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}$ (6); R = Me, R' = Ph. Examples of (III) which give type (II): R = Ph, R' = $p\text{-C}_6\text{H}_4\cdot\text{OMe}$; R = Ph, R' = $p\text{-C}_6\text{H}_4\text{Me}$; R = $\beta\text{-C}_{10}\text{H}_7$, R' = Ph; R = $p\text{-C}_6\text{H}_4\cdot\text{OMe}$, R' = $p\text{-C}_6\text{H}_4\text{Me}$; R =

$p\text{-C}_6\text{H}_4\text{Ph}$, $\text{R}' = \text{Ph}$; $\text{R} = p\text{-C}_6\text{H}_4\text{CH}:\text{CH}$, $\text{R}' = \text{Ph}$; $\text{R} = \text{Ph}$, $\text{R}' = p\text{-C}_6\text{H}_4\text{NO}_2$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$. The following substances are new: *p*-anisyl *p*-methylstyryl, m.p. 126°, and β -naphthyl styryl ketone, m.p. 106°; *o*-hydroxyphenyl $\alpha\beta$ -dibromo- β -phenylethyl, m.p. 192°; *p*-anisyl $\alpha\beta$ -dibromo- β -*p*-tolylethyl, m.p. 169°, *p*-anisyl α -bromo-*p*-methylstyryl, m.p. 129°, β -naphthyl $\alpha\beta$ -dibromo- β -phenylethyl, m.p. 173°, and β -naphthyl α -bromostyryl ketone, m.p. 116°; *p*-anisoyl-*p*-toluoyl, m.p. 104°, and benzoyl- β -naphthoyl-methane, m.p. 99°; 3-*p*-anisyl-5-*p*-tolyl, m.p. 148°, 5-*p*-anisyl-3-*p*-tolyl, m.p. 130°, 5-phenyl-3-*o*-hydroxyphenyl-, m.p. 231°, 3-phenyl-5-(3':4'-methylenedioxyphenyl)-, m.p. 130°, 3-phenyl-5-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 157°, 5-phenyl-3-(6'-bromo-3':4'-methylenedioxyphenyl)-, m.p. 179°, 3-phenyl-5- β -naphthyl-, m.p. 160°, and 5-phenyl-3- β -naphthyl-isooxazole, m.p. 152°.

F. R. S.

Analogues of ephedrine and adrenaline containing the morpholine nucleus and their esters. N. RUBIN and A. R. DAY (J. Org. Chem., 1940, 5, 54—60).—Amended instructions are given for the prep. of CH_2BzBr , CHBzMeBr , and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ from PhOMe and 3:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ from $o\text{-C}_6\text{H}_4(\text{OH})_2$. An excess of morpholine (I) and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ give morpholine hydrobromide and, after treatment with HCl , 4- β -phenylethylmorpholine hydrochloride, m.p. 246° (corr.). ω -Morpholinoacetophenone hydrochloride (II), m.p. 222—223° (corr.; decomp.), is obtained similarly or from equiv. amounts of (I) and CH_2BzBr in boiling EtOH containing a slight excess of anhyd. K_2CO_3 . α -Morpholinopropiophenone hydrochloride, m.p. 224° (corr.; decomp.), *p*-hydroxy- ω -morpholinoacetophenone, m.p. 201—201.7° (corr.) [hydrochloride, m.p. 242—243° (corr.; decomp.)], and 3:4-dihydroxy- ω -morpholinoacetophenone, m.p. 207° (corr.; decomp.) [hydrochloride, decomp. 224—225° (corr.)], are described. Reduction (10% $\text{Pd}\cdot\text{C}$ in EtOH) of the requisite ketone affords the following: β -morpholino- α -phenylethanol, m.p. 80.9—81.3° (corr.) [hydrochloride (III), m.p. 188—188.7° (corr.)]; β -morpholino- α -phenylpropanol, m.p. 73—73.5° (corr.) [hydrochloride (IV), m.p. 235° (corr.)]; β -morpholino- α -*p*-hydroxyphenylethanol hydrochloride, m.p. 178° (corr.; decomp.); β -morpholino- α -3:4-dihydroxyphenylethanol hydrochloride, decomp. 250° (corr.). The benzoate, m.p. 173.5—175° (corr.), and cinnamate, m.p. 220—221° (corr.), of (III) and the benzoate, m.p. 210—211° (corr.), of (IV) are described. (II), KCN , and $(\text{NH}_4)_2\text{CO}_3$ in 50% EtOH at 55—65° afford 5-phenyl-5-morpholinomethylhydantoin, m.p. 204—204.5° (corr.) [hydrochloride, m.p. 206° (corr.; decomp.)]. The other ketones do not yield hydantoin by this method.

H. W.

Oxazines.—See B., 1940, 30.

Ethyl α -keto- δ -2-benzoxazolyl- Δ^7 -pentenoate. W. DOELLER (Ber., 1939, 72, [B], 2148—2150).—Gradual addition of crotonyl chloride to $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ in abs. Et_2O at room temp. gives *o*-crotonamidophenol, m.p. 133—135°, transformed by distillation with P_2O_5 into 2-methyl- (I), m.p. 68—70°, and 2- Δ^7 -propenyl- (II), b.p. 121—123°/vac., -benzoxazole. (II) is obtained more simply and in

better yield by heating $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ with crotonic anhydride at 150° and subsequent distillation under atm. pressure. (II) condenses readily with $\text{Et}_2\text{C}_2\text{O}_4$ in presence of $\text{K}\cdot\text{Et}_2\text{O}\cdot\text{EtOH}$ at 0° to *Et* α -keto- δ -2-benzoxazolyl- Δ^7 -pentenoate, m.p. 146—148°. It follows therefore that Me when separated from the heterocyclic nucleus by $\cdot\text{CH}:\text{CH}\cdot$ has the same activity as in (I).

H. W.

Structural chemistry. I. The Ni^{++} specific group. H. ERLÉNMEYER and H. UEBERWASSER (Helv. Chim. Acta, 1940, 23, 197—206).— $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{N}\cdot\text{OH}$ with $\text{CS}(\text{NH}_2)_2$ in hot COMe_2 gives 2-amino-4-thiazolyl *Me* ketoxime, m.p. 194°, and with $\text{HCS}\cdot\text{NH}_2$ in $\text{Et}_2\text{O}\cdot\text{COMe}_2$ gives 4-thiazolyl *Me* ketoxime (I), m.p. 153—154°, hydrolysed by $\text{NaHSO}_3\cdot\text{AcOH}$ to 4-acetylthiazole, m.p. 56°. Bromination of $\text{COPh}\cdot\text{COMe}$ gives an oil, which with $\text{HCS}\cdot\text{NH}_2$ in Et_2O yields 4-benzoylthiazole, m.p. 49.5°, the oxime of which exists in forms (II), m.p. 104—105° and (III) 174—175°. $\text{COMe}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$ gives a Br-derivative, m.p. 143°, converted by $\text{HCS}\cdot\text{NH}_2$ into (III). Ni^{++} does not form a complex with (I), (II), or (III), for which failure an electronic explanation is offered.

R. S. C.

Benzthiazyl sulphides.—See B., 1940, 30.

Benzthiazyl alkyl sulphides.—See B., 1940, 119.

Cyanine types.—See B., 1940, 121.

2-Methyl-1-benzthiazolonemethide and 1:3:3-trimethyl-2-indolinonemethide usually designated "Fischer's base." O. MUMM, H. HINZ, and J. DIEDERICHSEN (Ber., 1939, 72, [B], 2107—2120).—1:3:3-Trimethyl-2-indolinonemethide (I),

$\text{C}_6\text{H}_4\langle\text{CMe}_2\text{NMe}\rangle\text{C}\cdot\text{CH}_2$, b.p. 248°/760 mm., 119°/12 mm., is unimol. as vapour or in freezing C_6H_6 . Methylbenzthiazole is converted by Me_2SO_4 into the methylsulphate, m.p. 135°, transformed by NaOH in 71% yield into 2-methyl-1-benzthiazolonemethide (II), m.p. 167° (picrate, m.p. 121—122°), now shown to be bimol. and hence

$\text{C}_6\text{H}_4\langle\text{S}\text{NMe}\rangle\text{C}\langle\text{CH}_2\text{NMe}\rangle\text{C}\langle\text{S}\text{NMe}\rangle\text{C}_6\text{H}_4$. The similarity of (I) to the pyridonemethides is shown by the formation of adducts, $\text{C}_{13}\text{H}_{15}\text{NS}_2$, $\text{C}_{19}\text{H}_{20}\text{N}_2\text{S}$, and $\text{C}_{19}\text{N}_{20}\text{ON}_2$, m.p. 171°, 158°, and 135°, respectively, with CS_2 , PhNCS , and PhNCO whilst (II) gives the adduct $\text{C}_{10}\text{H}_9\text{NS}_3$ with CS_2 . MgEtBr and (I) afford 1:2:3:3-tetramethyl-2-ethylindolenine, b.p. 89—90°/0.6 mm. (picrate, m.p. 166°). (I) and CNBr in EtOH at room temp. give the substance, $\text{C}_{13}\text{H}_{15}\text{N}_2\text{Br}$, m.p. 107—108°, converted by conc. HCl at 120° into the

compound, $\text{C}_6\text{H}_4\langle\text{CMe}_2\text{N}(\text{MeCl})\rangle\text{C}\cdot\text{CH}_2\text{Cl}$ (picrate, m.p. 134—135°). (I) is hydrogenated (PtO_2 in AcOH) to 1:2:3:3:3-tetramethyl-1:2:3:4:5:6:7-heptahydroindole, b.p. 90°/16 mm. (picrate, m.p. 177°). Freshly prepared (I) in EtOH is slowly converted by moist O_2 into the amine oxide, which could not be distilled without decomp. When heated at 150°/12 mm. 83% of it is volatilised as (I), identified as the picrate, m.p. 148°, and perchlorate, m.p. 195°, whilst the residue is converted into an isomeride (III),

$\text{C}_6\text{H}_4\langle\text{CMe}_2\text{C}(\text{CH}(\text{OH}))\text{C}\rangle\text{C}_6\text{H}_4$, m.p. 83°. (III) is obtained in 50% yield if the oxide is warmed at 134°/atm. pressure for some hr. previous to distillation and also by the action of 3% H_2O_2 on a solution of (I) in C_6H_6 at 30°. The re-formation of (I) from the oxide is not accompanied by the liberation of O_2 since no gas is evolved when it is heated at 200—260°/vac. whereby, however, the substance, $\text{C}_6\text{H}_4\langle\text{CMe}_2\text{C}(\text{CH}_2\text{CO})\text{C}\rangle\text{C}_6\text{H}_4$, m.p. 225—227°, is produced. Dry (II) is not affected by dry O_2 but with the moist gas autoxidation yields the compound, $\text{C}_6\text{H}_4\langle\text{S}\text{C}(\text{CH}_2\text{OH})\text{C}(\text{OH})\text{S}\rangle\text{C}_6\text{H}_4$, m.p. 171°. The corresponding Me_2 ether, m.p. 162°, is obtained by autoxidation of (II) in abs. MeOH .

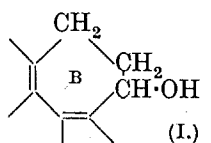
H. W.

Lycoris alkaloids. XIV. Constitution of lycorine. VI. H. KONDO and H. KATSURA (Ber., 1939, 72, [B], 2083—2088).—Dihydrolycorine (I) is converted by excess of MeI into the *methiodide*, decomp. 282—283°, which with AgCl gives the non-cryst. *methochloride* (corresponding *platinichloride*, m.p. 288°) not reduced by 5% $\text{Na-Hg-H}_2\text{O}$. With Ac_2O and anhyd. NaOAc at 100° (I) yields *diacetyldihydrolycorine*, m.p. 175°, transformed by BrCN in C_6H_6 at 100° into the *bromocyanide* (II), m.p. 176°. (II) is not hydrogenated in presence of Pd-CaCO_3 , Pd-C , or Pt-C on EtOH . It is converted by hot N-KOH-EtOH into the neutral *cyanodihydrolycorine anhydride* (II), $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N-CN}$, m.p. 217°, also (+1 EtOH) m.p. 182° (*Ac* derivative, m.p. 236°), which does not react with $\text{C}(\text{NO}_2)_4$ or KMnO_4 , and a syrup which when further treated with N-KOH or 30% H_2SO_4 gives *dihydronorlycorine anhydride*, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{NH}$, m.p. 198°, also (+1 H_2O) m.p. 204° (*Ac* derivative, m.p. 167—168°), which gives Liebermann's nitroso-reaction. Oxidation (CrO_3 in AcOH) of (II) at 45° yields *ketodihydronorlycorinone anhydride*, decomp. 341° (*monoxime*, decomp. 293—295°), which does not react with FeCl_3 , PhCHO , or diazonium compounds. It is converted by Me_2SO_4 and NaOH into the *Me* derivative, m.p. 258°, which is not sol. in NaOH , is free from OMe , and gives a *monoxime*, decomp. 266—268°.

H. W.

Dihydroergotocine.—See B., 1940, 173.

Colchicine and related compounds. I. Structure of colchicine. A. COHEN, J. W. COOK, and (Miss) E. M. F. ROE. II. **Synthesis of a simple analogue of N-acetylcolchicinol methyl ether.** J. W. COOK and L. L. ENGEL (J.C.S., 1940, 194—197, 198—200).—I. Colchicinol *Me* ether and HNO_2 give a *carbinol*, $\text{C}_{19}\text{H}_{22}\text{O}_5$, m.p. 115.5—116.5° (*p-phenylbenzoate*, m.p. 146—147°), which in some preps. is contaminated with a by-product, m.p. 133—134°.



The *carbinol* does not react with $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ in boiling C_6H_6 but at 180°, a *H phthalate*, m.p. 143—144°, is obtained. From ultra-violet absorption measurements the substance is not a phenanthrene derivative. It is suggested that the ring B of colchic-

ine (Windaus, A., 1924, i, 1089) may be seven-membered, leading to the structure (I) for the *carbinol*.

II. 3:4:5:1-(OMe) $_3\text{C}_6\text{H}_2\text{CHO}$ (II) (*anil.* m.p. 89—90°) and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ in Ac_2O give α -*phenyl-β*-(3:4:5-trimethoxyphenyl)acrylic acid, m.p. 186—187° (*p-phenylphenacyl* ester, m.p. 123.5—124.5°), which is hydrogenated (Pd-C) to the corresponding propionic acid, b.p. 215—219°/0.5 mm. (*p-phenylphenacyl* ester, m.p. 94—95°), also obtained by hydrolysis of α -cyano- α -phenyl-β-(3:4:5-trimethoxyphenyl)ethylene, m.p. 77—79° [from $\text{CH}_2\text{Ph}\cdot\text{CO-CN}$ and (II)]. $\text{Na p-anisylacetate}$ and (II) in Ac_2O afford α -*p-anisyl-β*-(3:4:5-trimethoxyphenyl)acrylic acid, m.p. 207—208° (*Et* ester, m.p. 84—85°; *p-phenylphenacyl* ester, m.p. 169—170°), 3:4:5:4'-tetramethoxy-stilbene, b.p. 159.5—160.5°, and the *anhydride* of anisyltrimethoxyphenylacrylic acid, m.p. 143—144°. Hydrogenation (PtO_2) of the acrylic acid yields α -*p-anisyl-β*-(3:4:5-trimethoxyphenyl)propionic acid, m.p. 95.5—96.5° (*p-phenylphenacyl* ester, m.p. 94—95°). *p-Anisylacetone* nitrile and (II) in EtOH-NaOH give α -cyano- α -*p-anisyl-β*-(3:4:5-trimethoxyphenyl)ethylene, m.p. 114—115°, which on reduction ($\text{H}_2\text{-PtO}_2$) affords a mixture of the *ethane*, m.p. 96.5—97.5°, and β -*p-anisyl-γ*-(3:4:5-trimethoxyphenyl)propylamine (*p-C}_6\text{H}_4\cdot\text{SO}_2 derivative, m.p. 135—136°; β - $\text{C}_{10}\text{H}_7\cdot\text{SO}_2$ derivative, m.p. 129.5—131°), isolated as the *N-Ac* compound, m.p. 124.5—125.5°; this substance may have a structural relationship to a colchicine degradation product.*

F. R. S.

Cinchona alkaloids. XXXI. Characterisation and preparation of epiquinine and epiquinidine. P. RABE and H. HÖTER (J. pr. Chem., 1939, [ii], 154, 66—72; cf. A., 1939, II, 187).—The mixture obtained from quinine or quinidine by $\text{KOH-C}_5\text{H}_{11}\cdot\text{OH}$ at 142° is separated by removing the quinine as sulphate, then the quinidine as *H d-tartrate*, and next separating from H_2O a compound (I), *epiquinine, epiquinidine*, H_2SO_4 , +6 H_2O (47.5%), sinters at ~100°, m.p. 101—103°, decomp. ~115°, $[\alpha]_D^{20}$ +38.5° in H_2O . With NH_4CNS in EtOH , (I) gives *epiquinidine* (68% yield), m.p. 113° [*hydrobromide*, + H_2O , m.p. 240° (slow heating; later decomp.)], as *thiocyanate*, m.p. 193°, $[\alpha]_D^{20}$ +44.5° in H_2O ; the residual bases yield *epiquinine* (77%) (*thiocyanate*, an oil) as *hydrobromide*, +3 H_2O , m.p. 71—77° (decomp. at ~108°), $[\alpha]_D^{20}$ +32.9° in H_2O .

R. S. C.

Strychnos alkaloids. CVIII. Catalytic hydrogenation of dibromohydroxynucine and related C_{17} compounds. H. LEUCHS and H. L. LOUIS (Ber., 1939, 72, [B], 2076—2079).—The salt $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_2\text{Br}_2\cdot\text{HBr}$ rapidly absorbs 4 H and then, more slowly, an additional 0.8 H, giving 3-bromo-2-hydroxydihydronucine, m.p. 252° (vac.; decomp.) after much darkening at 225—240° (*hydrobromide*, $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}_2\text{Br}\cdot\text{HBr}$, $[\alpha]_D^{20}$ +43.3°/d; *methiodide*, decomp. ~265° after becoming brown at 255°), also obtained by hydrogenation of 3-bromo-2-hydroxynucine. Similarly the *methobromide*, $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_2\text{Br}_2\cdot\text{MeBr}$, is hydrogenated (PtO_2 in H_2O) to the compound, $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}_2\text{Br}\cdot\text{MeBr}$, m.p. >300° after becoming black at 240° (corresponding *methoperchlorate*). Under similar conditions nucine gives

only dihydronucine, isolated as the *perchlorate*, $C_{17}H_{24}O_2N_2 \cdot 1.5HClO_4$, and 2-hydroxynucine affords 2-hydroxydihydronucine, m.p. 188—190° (decomp.).

H. W.

Solasodine. III. H. ROCHELMMEYER [in part, with H. CHEN] (Arch. Pharm., 1939, **277**, 329—339; cf. A., 1937, II, 356).—Solasodine (I) is identical with solanecarpidine and is shown to contain the 3-hydroxy-10-methyl- Δ^5 -polyhydrocyclopentanophenanthrene nucleus (OH and Me *cis*). After prep. from *Solanum xanthocarpum* it is obtained anhyd. from dry $COMe_2$ or $EtOAc$ and then has the formula, $C_{27}H_{43}O_3N$ (cf. lit.), m.p. 197—198°, and $[\alpha]_D^{20} -92.4^\circ$ in C_6H_6 , contains 2 active H (MgMeI), gives sterol colour reactions, with $BzCl$ or $Ac_2O-C_5H_5N$ gives a *monobenzoate*, m.p. 216—217°, or *acetate*, m.p. 193—194° [with hot 1% KOH-MeOH regenerates (I)] (neither ester gives a digitonide), respectively, is quantitatively pptd. by digitonin, is hydrogenated (PtO_2 , $AcOH$; 2 H_2) to a *substance*, m.p. 286.5—288° (block), $[\alpha]_D^{25} -4.94^\circ$ in $CHCl_3$ (*digitonide*), is oxidised by $Al(OBu^v)_3$ in $COMe_2$ to the Δ^4 -ketone, $C_{27}H_{41}O_2N$, m.p. 184—185°, $[\alpha]_D^0$ [no digitonide; absorption max. at 232 ($\log \epsilon$ 4.18) and 270—280 $m\mu$. (ϵ low)], and is dehydrated by Al_2O_3 to a mixture of dienes, which, when repeatedly crystallised or when heated with HCl-MeOH, gives the $\Delta^{3:5}$ -diene, solanosodine (II), m.p. 174—175°, $[\alpha]_D^{17} -195^\circ$ in $CHCl_3$. (II) is obtained also in small amount during the prep. of (I), gives the Rosenheim reaction, and has an absorption max. at 234 $m\mu$. ($\log \epsilon$ 4.34). R. S. C.

Solatubin. IV. H. ROCHELMMEYER [in part, with C. S. SHAH and E. GEYER] (Arch. Pharm., 1939, **277**, 340—355; cf. A., 1938, II, 151).— α -Cholesterol oxide and SO_2 in hot, aq. EtOH give cholestanetriol, m.p. 236° (best method of prep.; diacetate, m.p. 165—167°). Solatuberyl acetate (I) and BzO_2H in $CHCl_3$ give a poor yield of the *N*-oxide, m.p. 263—265° (decomp.), reconverted into (I) by SO_2 . Solatubin (II) is rapidly hydrogenated (PtO_2) in $AcOH$, but (I) is much more resistant, even in presence of much PtO_2 . $Al(OPr^i)_3$ or $Al(OBu^v)_3$ in $COMe_2-C_6H_6$ oxidises (II) to Δ^4 -solatubenone (III), m.p. 216° [absorption max. at 236 $m\mu$. (ϵ 17,000)], stable to HCl-EtOH, reduced by $Zn-Hg-HCl-AcOH$ to Δ^4 -solatubene, $C_{27}H_{43}N$ (~30% yield), m.p. 164°, $[\alpha]_D^{20} +32.4^\circ$ in C_6H_6 , by $Na-C_5H_{11}OH$ to solatubanol, and by $Na-EtOH$ to Δ^4 -solatubenol. One product of the reduction of (III) by $Al(OPr^i)_3$ (*loc. cit.*) is Δ^4 -trans-solatubenol, $C_{27}H_{43}ON$, m.p. 169—170°, $[\alpha]_D^{19} +116.4^\circ$ in $CHCl_3$ (no digitonide; Rosenheim reaction), converted by $Al(OBu^v)_3-COMe_2-C_6H_6$ into trans-solatubanone, $C_{27}H_{43}ON$, m.p. 214° (corr.), $[\alpha]_D^{19} +48.9^\circ$ in C_6H_6 [no digitonide; semicarbazone, m.p. 237°; absorption max. at 275 $m\mu$. ($\log \epsilon$ 1.65)]. This is reduced by H_2-PtO_2 in $AcOH$ at 60—70° to solatubanol, but in presence of a little HBr to trans-solatubanol, $C_{27}H_{45}ON$, m.p. 192°, $[\alpha]_D^{19} +20.65^\circ$ in $CHCl_3$ (no digitonide). The solatubadiene obtained from (II) by Al_2O_3 is the $\Delta^{3:5}$ -diene [absorption max. at 228 (ϵ 23,900) and 234 $m\mu$. (ϵ 24,400)]. The $\Delta^{2:4}$ -diene, m.p. 178°, $[\alpha]_D^{18} +139^\circ$ in C_6H_6 [absorption max. at 265 and 275 $m\mu$. (ϵ 6700)], is obtained from Δ^4 -cis-solatuberyl benzoate by $NPhMe_2$ at 200—230°,

by aq. (30% yield) or alcoholic (1% yield) acid. Solatubin acetate is similarly dehydrated by acid hydrolysis, but neither acid nor alkali causes dehydration of cholesteryl acetate. R. S. C.

Benziminazolearsinic acids etc.—See B., 1940, 173.

Mercuriphenyl 3-nitrophthalate, naphthalate, and dinitrophthalate.—See B., 1940, 173.

Micro-determination of carbon by the wet method. E. F. DEGERING and T. Z. BALL (Ind. Eng. Chem. [Anal.], 1940, **12**, 124—125).—The sample is oxidised with CrO_3 in H_2SO_4 and the vol. of CO_2 evolved is measured with a Hg dilatometer. Apparatus and procedure are detailed. J. D. R.

Apparatus for determining total carbon.—See A., 1940, III, 274.

Qualitative test for oxygen in organic compounds. D. DAVIDSON (Ind. Eng. Chem. [Anal.], 1940, **12**, 40—41).—The test for O in compounds free from N and S is based on the solubility of Fe^{III} hexathiocyanatoferrate ("thiocyanate") in O derivatives and insolubility in hydrocarbons and their halogen derivatives. Test paper is prepared by impregnating filter-paper with a solution of $FeCl_3$ and KCNS in MeOH. The paper is stirred with the test substance, if liquid (if solid, with a solution in a hydrocarbon or halogenated hydrocarbon), and the presence of O is indicated by development of a red colour in the liquid. Only substances free from N and S may be used. J. D. R.

Direct determination of oxygen in organic substances etc.—See A., 1940, I, 173.

Rapid micro-Kjeldahl method. A. KEYS (J. Biol. Chem., 1940, **132**, 181—187).—The micro-apparatus described yields results of accuracy comparable with those obtained by the ordinary Kjeldahl method. N can be determined in 0.1—0.2 c.c. of serum. The distillation is effected under slightly reduced pressure. P. G. M.

Determination of sulphur in organic compounds. E. W. D. HUFFMAN (Ind. Eng. Chem. [Anal.], 1940, **12**, 53—58).—Apparatus and detailed procedure are described for the determination of S in compounds containing no elements other than C, H, O, N, and S. The oxides of S formed in the combustion react with Ag pellets, with quant. formation of Ag_2SO_4 , which is determined by electro-deposition as Ag from dil. aq. Pr^2OH solution. C and H vals. may be obtained simultaneously. J. D. R.

Determination of iron in iron salts of organic acids containing phosphorus. C. F. BICKFORD, A. E. JURIST, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1939, **28**, 1028—1029).—Org. matter is destroyed by digestion with $H_2SO_4-H_2O_2$ and Fe is pptd. by H_2S -aq. NH_3 ; the ppt. is converted into $Fe(OH)_3$, ignited, and weighed. The method is applicable in some instances (*e.g.*, Fe adenylate) without removal of org. matter. F. O. H.

Wijs iodine values for conjugated double bonds. Influence of sample-reagent ratio. W. C. FORBES and H. A. NEVILLE (Ind. Eng. Chem.

[Anal., 1940, 12, 72—74).—I vals. obtained (Wijs) for substances with conjugated double linkings are strongly influenced by the excess amount of the reagent, and data are given to show this effect for Δ^6 -linoleic acid, tung oil, and dehydrated castor oil. Excess of reagent is of only slight importance for isolated systems, e.g., Δ^2 -linoleic acid, $\Delta^{2,5}$ -linolenic acid, and raw castor oil. To obtain comparable I vals. with substances containing conjugated double linkings, it is suggested that the ratio of vol. of reagent to wt. of sample be kept const. and a test for conjugated double linkings is suggested by determination of the I val. at varying ratios of reagent : sample.

J. D. R.

Analytical procedures employing Karl Fischer reagent. II. **Determination of alcoholic hydroxyl.** W. M. D. BRYANT, J. MITCHELL, jun., and D. M. SMITH. III. **Determination of organic acids.** J. MITCHELL, jun., D. M. SMITH, and W. M. D. BRYANT (J. Amer. Chem. Soc., 1940, 62, 1—3, 4—6; cf. A., 1939, I, 577).—A quant. method for the determination of OH-compounds, applicable to aliphatic and alicyclic alcohols, including branched-chain types and OH-acids, and aromatic alcohols which have OH attached to an aliphatic side-chain, depends on the determination of H_2O , liberated by interaction of the OH-compound with AcOH, by titration with the Karl Fischer reagent. Data are recorded for 25 compounds, and aq. EtOH solutions of various concns. have also been analysed. *tert.*-Aliphatic alcohols can be analysed by this procedure, but phenols do not esterify completely under the general working conditions. The procedure for the approx. determination of aliphatic in presence of aromatic alcohols is based on the use of more dil. catalyst solutions. Aldehydes, ketones, acetals, ketals, and amines interfere.

III. A method, based on the complete esterification and subsequent titration of the liberated H_2O by Karl Fischer reagent, is quant. for the determination of carboxylic acids. The method is applicable to aliphatic acids, including branched-chain and OH-substituted types, and aromatic acids having the CO_2H attached to an aliphatic side-chain. Analytical data are recorded for 18 acids. Changes in the concn. of catalyst solution affect the esterification considerably. A method for the determination of aliphatic in presence of aromatic acids is based on the large differences in esterification rates. *tert.*-Alcohols, H_2SO_4 , and anhydrides interfere.

W. R. A.

Determination of formaldehyde. II. **Ammonia method.** A. FOSCHINI and M. TALENTI (Z. anal. Chem., 1939, 118, 94—97; cf. A., 1939, II, 463).—Details of procedure and apparatus for determining CH_2O by adding an excess of $2N-NH_3$, shaking, and allowing time for $(CH_2)_6N_4$ to form, and distilling the excess of NH_3 into $N-H_2SO_4$ under reduced pressure, are given. The results agree with those obtained by the H_2O_2 method (*loc. cit.*), but are > those given by the indirect titration of NH_3 .

L. S. T.

Determination of acetone. M. W. GREEN (J. Amer. Pharm. Assoc., 1940, 29, 33—35).—The

method of pptn. as Hg complex and the oxime method do not give accurate or reproducible results. The CHI_3 method (U.S.P. XI) gives uniform but high (by 0.18—0.55% for 0.02 g. of $COMe_2$) vals., probably owing to a secondary reaction in which formate is produced.

F. O. H.

Potentiometric titration of glucose with alkaline tartrate solutions of copper, including Fehling's solution. H. T. S. BRITTON and L. PHILLIPS (Analyst, 1940, 65, 18—24).—Although the oxidation follows no definite stoichiometric reaction, completion occurs when the Cu^{++} ions are removed, and this is indicated by a rapid diminution in the potential recorded at a Pt electrode immersed in the solution. The ratio of CuO to glucose is only slightly affected by changes in the concn. of tartrate, but is markedly dependent on the p_H of the solution and the concn. of the glucose. The val. of methylene-blue as an internal indicator (cf. J.S.C.I., 1923, 42, 32*r*) is confirmed.

E. C. B. S.

Determination of glucose and fructose in presence of pentoses.—See A., 1940, III, 370.

Effect of iodine and mercury on amino-nitrogen values with nitrous acid. A. B. KENDRICK and M. E. HANKE (J. Biol. Chem., 1940, 132, 739—751; cf. A., 1937, III, 108).—The results of Dunn *et al.* (A., 1938, II, 125) are not confirmed. With glycine, addition of I' gives a correct val. for NH_2-N , either manometrically or volumetrically (Hg present or absent), and the effect of I' is therefore not through a HgI_2 complex; $Hg(OAc)_2$ lowers the NH_2-N val. to theoretical, and Hg to 103% theoretical. With cystine, added I' gives a normal val. volumetrically; $Hg(OAc)_2$ and Hg cause increases from 108% to 140% theoretical. With glycylglycine and glutathione, added I' somewhat improves the val. Both I' and $Hg(OAc)_2$ reduce the amount of CO_2 evolved in the glycine analysis, and increase that from cystine. Mechanisms are discussed. When KI is used in these analyses, it is best added with $NaNO_2$, not with AcOH.

E. W. W.

***p*-Dimethylaminobenzaldehyde method for determination of tryptophan compared with glyoxylic acid method.** J. L. D. SHAW and W. D. MACFARLANE (J. Biol. Chem., 1940, 132, 387—392).—The $p-NMe_2 \cdot C_6H_4 \cdot CHO$ method gives high results owing to the formation of coloured compounds with substances other than tryptophan. The $CHO \cdot CO_2H$ method is more reliable.

P. G. M.

Analytical behaviour of the group $\cdot CS \cdot NH \cdot$.—See A., 1940, I, 174.

Colorimetric determination of quinine.—See A., 1940, III, 275.

Reineckate and silicotungstate of narcotine; determination of narcotine. P. DUQUÉNOIS and M. ELLERT (Bull. Soc. chim., 1939, [v], 6, 1582—1586; cf. A., 1939, II, 398).—Narcotine hydrochloride in aq. HCl affords the *reineckate*, $[Cr(NH_3)_2(SCN)_4] \cdot C_{22}H_{23}O_7N$, and silicotungstate, $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 4C_{22}H_{23}O_7N$ (or $+7H_2O$). The latter is better for determining narcotine. A. T. P.

A., II.—Organic Chemistry

MAY, 1940.

Calculation of the number of stereoisomerides in carbon chain compounds. G. E. K. BRANCH and T. L. HILL (J. Org. Chem., 1940, 5, 86—99).—The method is applicable to straight- and branched-chain compounds containing asymmetric C atoms and/or double linkings (geometrical isomerism). The no. of optically inactive forms can also be calc.

H. B.

Physical properties of $\beta\beta\gamma$ -trimethylpentane.—See A., 1940, I, 154.

Isomerisation of hydrocarbons. IV. Isomeric butanes and their equilibrium mixtures. B. MOLDAVSKI and T. NIZOVKINA (J. Gen. Chem. Russ., 1939, 9, 1652—1660).—The sole reaction taking place when n -C₄H₁₀ is heated at 70—110° in presence of AlCl₃ is: n -C₄H₁₀ \rightleftharpoons *iso*-C₄H₁₀; at equilibrium the ratio $K_p = [\textit{iso}\text{-C}_4\text{H}_{10}]/[\text{C}_4\text{H}_{10}] = 611/T - 1.204$. At higher temp. cracking, with production of CH₄ and C₃H₈, takes place. R. T.

Manufacture of isobutane from n -butane.—See B., 1940, 190.

Catalytic dehydrogenation.—See B., 1940, 190.

Catalytic hydrogenation of trisubstituted ethylenes.—See A., 1940, I, 225.

Preparation and structure of polybutenes of high mol. wt. R. M. THOMAS, W. J. SPARKS, P. K. FROLICH, M. OTTO, and M. MUELLER-CUNRADI (J. Amer. Chem. Soc., 1940, 62, 276—280).—The following summary of results, partly described in patents, is illustrated with graphs but few experimental details. The rate of polymerisation of isobutenes (I) by acidic catalysts is independent of temp., but the mol. wt. increases with decreasing temp., e.g., from 10,000 at $\sim -25^\circ$ to 220,000 at -105° . The characteristic nature of the reaction is shown by occurrence of an induction period at the b.p. but not at -80° when BF₃ is the catalyst. Impurities, including n -C₄H₈ or higher olefines, reduce the mol. wt. of the product. Inert diluents moderate the reaction; with increasing amounts of diluent, the mol. wt. of the product rises to a sharp max. The amount of catalyst must usually exceed some crit. val. Yields are $>90\%$. Products are probably $[\text{C}\cdot\text{CMe}_2]_n$, containing a terminal ethylenic linking. Decomp. at 350° of a product having mol. wt. $\sim 20,000$ gives 50% of C₄- and 20% of C₈-compounds, including much CH₂:CMe·CH₂Bu^v (I) and possibly some CHBu^B:CMe₂. (I) is stable at 350° and polymerisation may thus be not entirely homogeneous.

R. S. C.

Isomerisation of unsaturated hydrocarbons in contact with oxides of metals. II. Isomer-

isation of diallyl in presence of chromic oxide. R. J. LEVINA and P. J. KIRIUSCHOV (J. Gen. Chem. Russ., 1939, 9, 1834—1840; cf. A., 1937, II, 331).—(CHMe:CH)₂ is obtained in 70—74% yield when diallyl is passed over Cr₂O₃ at 225—250°. R. T.

Catalytic hydrogenation polymerisation of acetylene.—See B., 1940, 190.

Preparation of methyl chloride from methyl sulphate and aluminium chloride. A. A. SCHAM-SCHURIN (J. Gen. Chem. Russ., 1939, 9, 2207—2208).—The reaction $3\text{Me}_2\text{SO}_4 + 2\text{AlCl}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{MeCl}$ takes place at room temp. R. T.

Reaction of alkyl halides with hydrogen halides and decomposition of methyl bromide. H. P. MEISSNER and H. J. SCHUMACHER (Z. physikal. Chem., 1940, 185, 435—446).—The thermal decomp. of MeBr and the reactions of MeBr and MeCl with HBr and HI have been studied. Decomp. of MeBr begins at 400—500°, according to the origin of the sample, presumably owing to the presence of traces of catalytically-active impurities. The volatile products are CH₄ and HBr, with some H₂ at lower temp.; liquid Br-compounds and C are also formed. The reaction is homogeneous, and is retarded by the products. Below the temp. of their decomp., MeBr and MeCl do not react with HBr. MeCl and HI react at 325° according to $\text{MeCl} + 2\text{HI} = \text{CH}_4 + \text{I}_2 + \text{HCl}$; the reaction is heterogeneous. The reaction between MeBr and HI is very complicated. F. J. G.

Action of fluorine on organic compounds. VII. Vapour-phase fluorination of ethyl chloride. J. D. CALFEE, N. FUKUHARA, DE W. S. YOUNG, and L. A. BIGELOW (J. Amer. Chem. Soc., 1940, 62, 267—269).—Passage of EtCl and F₂ over Cu gauze at 900° (cf. A., 1940, II, 62) gives CF₄, CClF₃, CF₃·CClF₂ (I), CCl₂:CF₂, m.p. -116° , b.p. 0° (lit. 15°), CH₂Cl·CH₂F (II), and higher-boiling products. Increasing the ratio F : EtCl from 1 : 1 to 2 : 1 decreases the amount of (II) in the products from 70 to 10% and increases the amount of (I) from a trace to 10%. Dilution with N₂ decreases the amount of the first four products named. Chlorination is brought about by ClF. Analysis of stable org. gases containing F and Cl is improved. R. S. C.

Action of fluorine on simple aliphatic chlorinated hydrocarbons. W. T. MILLER (J. Amer. Chem. Soc., 1940, 62, 341—344).—Nearly pure F₂ (A., 1936, 1350) and CHCl₃ at 0° give CCl₃F and a little C₂Cl₆. C₂HCl₅ at $90 \pm 3^\circ$ gives C₂Cl₅F, C₂Cl₆, and some (CCl₂F)₂, C₂Cl₄, and decachlorobutane, m.p. $80\text{--}81^\circ$. (CHCl₂)₂ at $50 \pm 2^\circ$ gives CH₂Cl·CCl₂F with smaller amounts of (CCl₂F)₂, C₂HCl₃, and C₂HCl₅. C₂Cl₄ at

0° gives mainly $(\text{CCl}_2\text{F})_2$, $\text{C}_2\text{Cl}_5\text{F}$, and *octachloro*- (? $\alpha\delta$)-*difluorobutane*, m.p. 4—5°, b.p. 152.5°/20 mm.; in $\text{C}_2\text{Cl}_3\text{F}_3$ much less CCl_5F is formed and a trace of C_2Cl_6 is also obtained. C_2HCl_3 at 0° gives $\text{CCl}_2\text{F}\cdot\text{CHClF}$, $\text{C}_2\text{Cl}_3\text{F}$, mixed $\text{C}_2\text{HCl}_3\text{F}$, a *hexachlorobutane*, m.p. 9.5—11°, b.p. 122—125.5°/25 mm., an *octachlorobutane*, m.p. 75—76°, and $(\text{CClF})_2$, b.p. 31—32°; in $\text{C}_2\text{Cl}_3\text{F}_3$ a *hexachlorodifluorobutane*, m.p. 55—56°, and other products are obtained. F_2 is almost insol. in these reactants, and reaction occurs in the vapour phase. This and the formation of ClF account for the "dimeride addition" products and other peculiarities differentiating fluorination from other halogenations. R. S. C.

Autoxidation of halogen-substituted ethylenes. E. PRIKLESHAeva and N. PRIKLESHAev (J. Gen. Chem. Russ., 1939, 9, 1766—1773).—Oxidation of $\text{CHX}\cdot\text{CX}_2$ or C_2X_4 ($\text{X} = \text{Cl}, \text{Br}$) by AcO_2H consists of the reactions: $\text{C}_2\text{HX}_5 \leftarrow (+\text{X}_2) \text{CHX}\cdot\text{CX}_2 \xrightarrow{(+\text{O})} \text{CHX}\cdot\text{CO} + \text{X}_2$; $\text{CO}_2 + \text{CO} + \text{HX} \leftarrow (+\text{O}_2) \text{CHX}\cdot\text{CO} (+\text{X}_2) \rightarrow \text{CHX}_2\cdot\text{CO}_2\text{H} + \text{HX}$; $\text{C}_2\text{X}_6 \leftarrow (+\text{X}_2) \text{C}_2\text{X}_4 \xrightarrow{(+2\text{O})} \text{CO}\cdot\text{CO} (+\text{O}_2) \rightarrow 2\text{CO}_2$; $\text{C}_2\text{X}_4 \xrightarrow{(+\text{O})} \text{CX}_2\cdot\text{CO} (+\text{X}_2) \rightarrow \text{CX}_3\cdot\text{CO}_2\text{H} + \text{HX}$. R. T.

Allylic rearrangements. X. Reproducibility of standard methods for preparation of butenyl bromide mixtures. W. G. YOUNG and K. NOZAKI (J. Amer. Chem. Soc., 1940, 62, 311—313).—Previous results (A., 1937, II, 480; 1938, II, 214) are duplicated, except for two which are explained and corr. HBr in AcOH and a trace of Bz_2O_2 at 15° equilibrates $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and $\text{CH}_2\cdot\text{CHMeBr}$ to a mixture, having the n expected from the resonance process; at room temp. in absence of Bz_2O_2 addition of HBr predominates. R. S. C.

Chlorination of hexinene in reactive solvents. II. R. O. NORRIS and G. F. HENNION (J. Amer. Chem. Soc., 1940, 62, 449—450; cf. A., 1939, II, 400).—The yields of *cis*- and *trans*- $\text{CBu}^a\text{Cl}\cdot\text{CHCl}$, $\text{CBu}^a\text{Cl}\cdot\text{CCl}_2$ (I), $\text{CBu}^a\text{Cl}_2\cdot\text{CH}_2\text{Cl}$, and $\text{CBu}^a\text{Cl}_2\cdot\text{CCl}_3$ obtained from $\text{CBu}^a\cdot\text{CH}$ and Cl_2 in 35% aq. HCl , 30% aq. H_2SO_4 or H_3PO_4 , and 22% HCl - MeOH are reported. (I) was previously reported as $\text{CBu}^a\text{Cl}_2\cdot\text{CH}_2\text{Cl}$. R. S. C.

Preparation of aliphatic nitrohydrocarbons. H. C. DE MAUNY (Bull. Soc. chim., 1940, [v], 7, 133—139).— MeNO_2 and heptaldehyde are condensed in MeOH containing KOH and the resulting salt is pptd. by NaOMe in MeOH ; after filtration and desiccation it is decomposed with $\alpha\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in Et_2O , thereby giving α -nitro-octan- β -ol, b.p. 135°/10 mm., in 95% yield. This is dehydrated by Ac_2O at 100° and finally at 120° (less advantageously by ZnCl_2) to α -nitro- Δ^a -octene, b.p. 118°/10 mm. (yield 80%), which is selectively hydrogenated (PtO_2 in COMe_2) to α -nitro-octane, b.p. 120°/30 mm., m.p. 15°. Under similar conditions lauraldehyde yields successively α -nitrodecan- β -ol, m.p. 32—33°, α -nitro- Δ^a -decene, b.p. 156°/1.5 mm., and α -nitrodecane, m.p. 70°. By use of EtNO_2 and Pr^aNO_2 in place of MeNO_2 it is possible to prepare β - and γ - NO_2 -compounds. H. W.

Synthesis of dinitroparaffins. L. W. SEIGLE and H. B. HASS (J. Org. Chem., 1940, 5, 100—105).

— $\text{NO}_2\cdot\text{CRR}'\cdot\text{CR}''\text{R}'''\cdot\text{NO}_2$ are obtained from $[\text{CRR}'\cdot\text{NO}_2]\text{Na}$ and $\text{NO}_2\cdot\text{CR}''\text{R}'''\text{Hal}$, but similar derivatives are not formed when primary NO_2 -compounds are used. Thus, Pr^aNO_2 (I) (in aq. EtOH - NaOH) with $\text{CMe}_2\text{Cl}\cdot\text{NO}_2$, b.p. 131° (corr.)/760 mm., $\text{CMe}_2\text{Br}\cdot\text{NO}_2$ (II), b.p. 150—152° (corr.)/760 mm., and (crude) $\text{CMe}_2\text{I}\cdot\text{NO}_2$ gives 6 (~9 when dry Na salt in abs. EtOH is used), 29, and 43%, respectively, of $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethylbutane (III), m.p. 208.4—209°, also obtained (14%) from (I), (II), and NaHCO_3 (20% excess) in boiling 80% EtOH . $\gamma\delta$ -Dinitro- $\gamma\delta$ -dimethylhexane, m.p. 78° [from $\text{CHMeEt}\cdot\text{NO}_2$ (IV) and $\text{CMeEtBr}\cdot\text{NO}_2$, b.p. 171° (corr.)/760 mm. (16%), or (crude) $\text{CMeEtI}\cdot\text{NO}_2$ (34%)], $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethylpentane, m.p. 88—88.6° [~8% from (IV) and (II); a little (III) is also formed], and 1-nitro-1- α -nitroisopropylcyclohexane, m.p. 140—141° [19% from nitrocyclohexane and (II)], are similarly prepared. The above $\text{NO}_2\cdot\text{CRR}'\text{Hal}$, $\text{CHMeBr}\cdot\text{NO}_2$, b.p. 146—152° (corr.)/760 mm., and $\text{CHEtBr}\cdot\text{NO}_2$, b.p. 159—164° (corr.)/760 mm., are prepared from the appropriate NO_2 -compound (in aq. NaOH) and halogen.

H. B.
Reactions of ferric chloride with methyl alcohol and methyl acetate and benzoate. II. M. T. DANGJAN (J. Gen. Chem. Russ., 1939, 9, 1907—1910; cf. A., 1939, II, 253).—Anhyd. FeCl_3 and MeOH , MeOAc , or MeOBz yield cryst. compounds, which decompose when heated, yielding MeCl . The reactions are: $\text{MeOH} + \text{FeCl}_3 \rightarrow \text{MeOH}\cdot\text{FeCl}_3$ (I) $\rightarrow \text{MeCl} + \text{FeCl}_2\cdot\text{OH}$; (I) $\rightarrow \text{FeMeCl}_2 + \text{HOCl}$ (subsidiary reaction); $\text{R}\cdot\text{CO}_2\text{Me} + \text{FeCl}_3 \rightarrow \text{R}\cdot\text{CO}_2\text{Me}\cdot\text{FeCl}_3 \rightarrow \text{MeCl} + \text{R}\cdot\text{CO}_2\cdot\text{FeCl}_2$. The double salts are completely dissociated in presence of H_2O . R. T.

Conjugated systems. VIII. Reaction of β -chloro- $\Delta^{\alpha\gamma}$ -butadiene with hypobromous acid, and the synthesis of chlorovinylethylene oxide. A. A. PETROV (J. Gen. Chem. Russ., 1939, 9, 2232—2243).—Chloroprene and HOBr yield β -chloro- δ -bromo- Δ^a -buten- γ -ol (I), b.p. 77—77.5°/10 mm. (acetate, b.p. 83°/10 mm.), which with Br in CHCl_3 gives β -chloro- $\alpha\beta\delta$ -tribromobutan- γ -ol, m.p. 69.5—71° (acetate, m.p. 72—73°), oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to β -chloro- $\alpha\beta\delta$ -tribromobutan- γ -one, b.p. 134°/10 mm. (I) and KOH at 130° give chloroprene oxide (II), b.p. 109.4—109.6°/750 mm., which with 2% H_2SO_4 yields γ -chloro- Δ^a -butene- $\alpha\beta$ -diol, b.p. 108.5°/10 mm. (diacetate, b.p. 103.5°/10 mm.), and this with Br in CHCl_3 gives γ -chloro- $\gamma\delta$ -dibromobutan- $\alpha\beta$ -diol, m.p. 112.5—114°. (II) and conc. HCl give $\beta\gamma$ -dichloro- Δ^a -buten- δ -ol, b.p. 72—73°/10 mm. (acetate, b.p. 81°/10 mm.), whilst with conc. HBr the product is β -chloro- γ -bromo- Δ^a -buten- δ -ol, b.p. 85—86°/10 mm. (acetate, b.p. 92.5—93.5°/10 mm.), converted by Br in CHCl_3 into β -chloro- $\beta\gamma\delta$ -tribromobutanol, b.p. 156—156.5°/10 mm. R. T.

β -Ethylenic alcohols. O. KIUN-HOUO (Ann. Chim., 1940, [xi], 13, 175—241).—Addition of the requisite aldehyde or ketone to $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$ (I) under specified conditions gives Δ^a -buten- α -ol, b.p. 114°, Δ^b -penten- β -ol, b.p. 115°, Δ^c -hexen- γ -ol, b.p. 130° and β -methyl- Δ^b -penten- β -ol, b.p. 120° (vals. of d and n also recorded). (I) and acetaldehyde or

crotonaldehyde afford respectively Δ^{α} -heptadien- δ -ol, b.p. 150—151°, and Δ^{α} -hexadien- γ -ol, b.p. 130—131°. $\text{CHMe}:\text{CH}:\text{CH}_2\cdot\text{MgBr}$ is obtained in very dil. solution and in presence of a large excess of Mg and reacts with $\text{R}\cdot\text{CHO}$, giving γ -methyl- Δ^{α} -penten- δ -ol, b.p. 125—126°, γ -methyl- Δ^{α} -hexen- δ -ol, b.p. 140—141°, γ -methyl- Δ^{α} -hepten- δ -ol, b.p. 55—56°/14 mm. (tetrabromide, m.p. 126°), and 8-phenyl- γ -methyl- Δ^{α} -buten- δ -ol, b.p. 122—123°/14 mm. Attempts to prepare $\text{CHPh}:\text{CH}:\text{CH}_2\cdot\text{MgBr}$ were fruitless but the corresponding chloride and MeCHO afford γ -phenyl- Δ^{α} -penten- δ -ol, b.p. 122—123°/14 mm. Dehydration of β -ethylenic alcohols always takes place with mediocre yields whatever method is employed and cannot be regarded as a method for preparing dienes or trienes. With Al_2O_3 at 300—330° about 40% of alcohol is recovered unchanged, about 6% is transformed into a mixture of hydrocarbons and about 50% is ruptured into propylene and aldehyde: $\text{OH}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2 \rightarrow \text{RCHO} + \text{CHMe}:\text{CH}_2$. $\text{OH}\cdot\text{CHMe}:\text{CH}_2\cdot\text{CH}:\text{CHMe}$ behaves similarly, at any rate qualitatively. A *tert.* alcohol $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ is dehydrated under these conditions to a conjugated diene whilst $\alpha\beta$ -diethylenic alcohols suffer simultaneous dehydration to trienes and scission; $\text{CH}_2\text{Ph}:\text{CH}_2\cdot\text{OH}$ and $\text{CH}_2\text{Ph}:\text{CHMe}:\text{OH}$ are dehydrated to $\text{CHPh}:\text{CH}_2$ and $\text{CHPh}:\text{CHMe}$, respectively. The xanthate method leads in all cases to apparently complex mixtures of diethylenic hydrocarbons in very small yield. The gaseous alcohols are slowly dehydrated without scission by NaHSO_4 at 175° but the hydrocarbon appears to be a mixture in which conjugated dienes predominate without being exclusive. $\alpha\beta$ -Ethylenic alcohols yield doubly conjugated trienes without scission. $\text{CH}_2:\text{CH}:\text{CHPh}:\text{CHMe}:\text{OH}$ and $\text{OH}:\text{CHPh}:\text{CHMe}:\text{CH}:\text{CH}_2$ (particularly the latter) in the liquid phase are readily dehydrated by KHSO_4 . Linear β -ethylenic alcohols are dehydrogenated by Cu at 300° to saturated ketones, H becoming attached to the double linking. Some formation of α -ethylenic ketone by migration of the double linking appears probable. The amount of H_2 evolved is always small in comparison with the quantity of ketone produced. An α -ethylenic ketone is obtained exclusively from $\text{CH}_2:\text{CH}:\text{CH}:\text{C}(\text{OH})\cdot\text{CH}:\text{CH}_2$. $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{OH}$ yields $\text{Pr}^{\alpha}\text{CHO}$ and crotonaldehyde and rather more H_2 is liberated than is the case with *sec.* alcohols. The behaviour of β -ethylenic alcohols resembles closely that of the α -compounds but the syntheses have purely academic interest. $\text{KOH}\cdot\text{EtOH}$ does not isomerise β - to α -ethylenic alcohols but with the alcohol $\text{CH}_2:\text{CH}:\text{CHPh}:\text{CHMe}:\text{OH}$ it causes a wandering of the double linking towards the nucleus with scission, proved by the isolation of $\text{CHPh}:\text{CHMe}$. OH of β -ethylenic alcohols is not as mobile as that of the saturated alcohols but $\alpha\beta$ -diethylenic alcohols are as easily etherified by hydracids (or PBr_3) as α -ethylenic alcohols. In the case of $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{CH}_2$ this reaction is accompanied by transposition to $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{CH}:\text{CH}:\text{CH}_2\text{Br}$. Migration of the terminal linking cannot be induced by heat alone but Bouis' method permits passage to the primary alcohol, $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{CH}:\text{CH}:\text{CH}_2\cdot\text{OH}$, which under the prolonged influence of $\text{KOH}\cdot\text{EtOH}$ passes into the

conjugated alcohol, $\Delta^{\beta\beta}$ -hexadien- α -ol, b.p. 77—78°/14 mm. β -Ethylenic alcohols add Br in CCl_4 , usually giving non-cryst. bromohydrins which are difficult to purify; $\alpha\beta\epsilon\zeta$ -tetrabromohexan- γ -ol, however, has m.p. 86°. $\alpha\beta$ -Dibromopentan- δ -ol is transformed by anhyd. KOH in Et_2O into 4-bromo-2-methyltetrahydrofuran, b.p. 47°/14 mm., in moderate yield. When heated with finely-divided KOH it passes into 2-methyl-2 : 5-dihydrofuran, b.p. 74—76°/atm. pressure. 4-Bromo-2-ethyltetrahydrofuran, b.p. 65—66°/14 mm., is converted by the successive action of Mg and MeCHO into 2-ethyl-4-vinyltetrahydrofuran, b.p. 125—127°/760 mm., and 2 : 2'-diethyl-3-tetrahydrofuryl, $(\text{CHEt}:\text{CH}_2 > \text{CH})_2$, b.p. 136—138°/14 mm. Raman spectra of the alcohols are recorded. H. W.

Action of sulphuric acid on *tert.*-dienols. S. ZONIS (J. Gen. Chem. Russ., 1939, 9, 2191—2195).— $\text{OH}\cdot\text{CMe}_2\cdot\text{C}:\text{C}:\text{CH}:\text{CH}_2$ is hydrogenated (Pd catalyst) to ϵ -methyl- $\Delta^{\alpha\gamma}$ -hexadien- ϵ -ol, b.p. 50—51°/12 mm. COMePr^{α} , Mg, and $\text{CBr}:\text{C}:\text{CH}:\text{CH}_2$ in Et_2O give ϵ -methyl- Δ^{γ} -octin- Δ^{α} -en- ϵ -ol, b.p. 65—66°/5 mm., hydrogenated as above to ϵ -methyl- $\Delta^{\alpha\gamma}$ -octadien- ϵ -ol, b.p. 78—80°/12 mm. The dienols with H_2SO_4 (8—20 hr. at 100°) yield 1 : 1-dimethyl-, b.p. 108—111°, and 1-methyl-1-propyl- $\Delta^{2:4}$ -cyclopentadiene, b.p. 78—82°/55 mm. R. T.

l-Citronellol. J. DÈUVRE (Bull. Soc. chim., 1940, [v], 7, 139—144).—An extended account of work already reported (A., 1939, II, 355). H. W.

(A) **Synthesis and dehydration of di-*sec.* and di-*tert.* glycols of the $\text{C}_n\text{H}_{2n+2}\text{O}_2$ series.** A. D. PETROV and P. S. SANIN. (B) **Dehydration over alumina of *tert.* alcohols of the $\text{C}_n\text{H}_{2n+1}\text{OH}$ series.** A. D. PETROV [with V. V. VLASOV, E. I. STANKEVITSCH, E. E. TICHONOVA, and S. M. KOMLEV]. (C) **Synthesis of *sec.* alcohols, and their dehydration over alumina.** A. D. PETROV [with I. G. SUMIN, Z. A. MEEROVITSCH, K. N. KUDRINA, and G. N. TICHONOVA (J. Gen. Chem. Russ., 1939, 9, 2129—2137, 2138—2143, 2144—2147)].—(A) $\text{MgBu}^{\beta}\text{Br}$ and Et_2 adipate (I) yield $\beta\lambda$ -dimethyldodecane- δ -diol (II), m.p. 52° (diurethane, m.p. 153°). $\beta\eta$ -Dimethyloctane- $\beta\eta$ -diol [from (I) and MgMeI], $\beta\iota$ -dimethyldodecane- $\beta\iota$ -diol, m.p. 62° (from Et_2 suberate and MgMeI), $\gamma\mu$ -dimethyltetradecane- $\gamma\mu$ -diol, m.p. 72·5° (from Et_2 sebacate and MgEtBr), $\epsilon\theta$ -di-n-butyl-dodecane- $\epsilon\theta$ -diol, m.p. 103° (from Et_2 succinate and $\text{MgBu}^{\alpha}\text{Br}$), $\epsilon\kappa$ -di-n-butyltetradecane- $\epsilon\kappa$ -diol, m.p. 91° [from (I) and $\text{MgBu}^{\alpha}\text{Br}$], $\epsilon\xi$ -di-n-butyloctadecane- $\epsilon\xi$ -diol, m.p. 69° (from Et_2 sebacate and $\text{MgBu}^{\alpha}\text{Br}$), and $\eta\pi$ -di-n-hexyldocosane- $\eta\pi$ -diol, m.p. 48° (from Et_2 sebacate and $\text{C}_6\text{H}_{13}\cdot\text{MgBr}$), are obtained similarly. The di-*tert.*-glycols are dehydrated by heating for 2—3 hr. with anhyd. $\text{H}_2\text{C}_2\text{O}_4$ at 150—180°, and yield, respectively, myrcene, $\beta\eta$ -dimethyl- $\Delta^{\beta\lambda}$ -octadiene, b.p. 156—158·5°, $\beta\iota$ -dimethyl- $\Delta^{\beta\theta}$ -decadiene, b.p. 77—79°/3 mm., $\gamma\mu$ -dimethyl- $\Delta^{\gamma\lambda}$ -tetradecadiene, b.p. 171·5—172°/6 mm., $\epsilon\theta$ -di-n-butyl- $\Delta^{\epsilon\theta}$ -dodecadiene, b.p. 168—170°/7 mm., $\epsilon\kappa$ -di-n-butyl- $\Delta^{\epsilon\kappa}$ -tetradecadiene, b.p. 201—202°/10 mm., and $\epsilon\xi$ -di-n-butyl- $\Delta^{\epsilon\xi}$ -octadecadiene, b.p. 231—232°/9 mm.

(B) $\text{COMe}\cdot\text{C}_6\text{H}_{13}\cdot n$ and $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{MgBr}$ in Et_2O give δ -methyl- Δ^{α} -decen- δ -ol, b.p. 143—145°/82 mm.,

which when passed over Al_2O_3 at 290–300° yields chiefly δ -methyl- Δ^8 -decadiene, b.p. 120–122°/74 mm., octane no. 84. The following alcohols and dienes are prepared similarly: $\beta\zeta\theta$ -trimethyl- Δ^8 -nonen- ζ -ol, b.p. 93–94°/5 mm., and Δ^8 -nonadiene, b.p. 78–80°/12–13 mm., $\beta\zeta\eta$ -trimethyl- Δ^8 -tridecen- ζ -ol, b.p. 149–151°/5 mm., and Δ^8 -tridecadiene, b.p. 115–117°/3 mm., cetene no. 28, $\beta\zeta\eta$ -trimethyl- Δ^7 -octen- ε -ol, b.p. 75–77°/3 mm., and Δ^7 -octadiene, b.p. 56–58°/3 mm.

(c) The following alcohols are synthesised by the Grignard reaction from the appropriate aldehydes, and when dehydrated over Al_2O_3 at 360–400° yield the corresponding olefins: $\beta\zeta\zeta$ -trimethylheptan- δ -ol, b.p. 95–97°/25 mm., yielding $\beta\zeta\zeta$ -trimethyl- Δ^7 -heptene, b.p. 145–147°, $\beta\zeta$ -dimethylheptan- γ -ol, b.p. 110–120°/200 mm., and $\beta\zeta$ -dimethyl- Δ^7 -heptene, b.p. 120–130°, β -methyldecan- δ -ol, b.p. 155–165°/90 mm., and Δ^8 -decene, b.p. 74°/4 mm., $\varepsilon\zeta$ -dimethylheptan- γ -ol, giving $\varepsilon\zeta$ -dimethyl- Δ^7 -heptene, b.p. 120–128°/753 mm. The results of this and the preceding studies indicate that dehydration of alcohols containing primary or *sec.* radicals is effected between the C to which OH is attached and the neighbouring atom attached to the radical of the highest mol. wt.

R. T.

Catalytic dehydration of amylene glycols. E. BEATI and G. MATTEI (Annali Chim. Appl., 1940, 30, 21–28).—Passage of pentane- $\alpha\beta$ -diol over kaolin (I), basic Al sulphate (II) or phosphate (III) at 300–400° yields mainly BuCHO , the catalysts being of decreasing efficiency in the order given; with (III), small amounts of pentadiene are produced. With (I) or (II), pentane- $\alpha\delta$ -diol yields methyltetrahydrofuran; with (III), $\Delta^{\alpha\gamma}$ -pentadiene (IV) is preferentially formed. With (I) or (II), pentane- $\alpha\zeta$ -diol gives tetrahydropyran; with (III), (IV) is the principal product. Butane- $\alpha\gamma$ -diol with (II) affords PrCHO (approx. 20% yield) and butylene and butadiene products. The mechanism of the changes is discussed.

F. O. H.

Chemistry of naturally occurring monoanhydrohexitols. II. Synthetic tetramethylstyracitol. W. FREUDENBERG and J. T. SHEEHAN (J. Amer. Chem. Soc., 1940, 62, 558–560; cf. A., 1937, II, 439).—Hydrogenation (Raney Ni) of tetramethylgluco-*d*-pyranose in aq. EtOH at 135°/85 atm. gives $\alpha\gamma\delta\epsilon$ -tetramethylsorbitol (I), b.p. 145° (bath)/2 mm., $[\alpha]_D^{25} + 10.3^\circ$ in EtOH, $+4.7^\circ$ in CHCl_3 , converted by 13% H_2SO_4 at 140°/vac. into tetramethyl- $\alpha\zeta$ -anhydrosorbitol, b.p. 115° (bath)/2 mm., $[\alpha]_D^{25} - 36.2^\circ$ (-36.5°) (no solvent), identical with tetramethylstyracitol, prepared from styracitol (II). This reverses the constitution assigned to (II) (*loc. cit.*). Methylation of (I) or sorbitol gives hexamethylsorbitol, b.p. 100° (bath)/1.5 mm., $[\alpha]_D^{25} + 1.97^\circ$ (no solvent). Tetramethylmannose gives similarly tetra-, b.p. 150° (bath)/2 mm., $[\alpha]_D^{25} + 20.7^\circ$ in EtOH, $+17.5^\circ$ in CHCl_3 , and hexamethylmannitol, b.p. 97° (bath)/2 mm., $[\alpha]_D^{25} + 12.53^\circ$ (12.46°) (no solvent) (also obtained from mannitol), and tetramethyl- $\alpha\zeta$ -anhydromannitol, b.p. 95° (bath)/2 mm., $[\alpha]_D^{25} + 30.6^\circ$ (no solvent), which is not identical with tetramethylpolygalitol, b.p. 80° (bath)/2 mm., $[\alpha]_D^{25} + 67.67^\circ$ (no solvent) (*cf. loc. cit.*).

R. S. C.

Reactions of free radicals with organic compounds containing atoms with unshared electron pairs. F. O. RICE, W. D. WALTERS, and P. M. RUOFF (J. Chem. Physics, 1940, 8, 259–262).—In the thermal decomp. of MeOEt at 448° and 473° and in the promoted decomp. of MeOEt by $(\text{NMe}_2)_2$ at 297° and 300° no trace of Me_2O was found. No NH_2Me was produced by the thermal decomp. of NH_2Pr^a at 650°/10 mm. These results indicate either that the reactions $\text{Me} + \text{ROR}' \rightarrow \text{ROMe} + \text{R}'$ and $\text{Me} + \text{NH}_2\text{R} \rightarrow \text{NH}_2\text{Me} + \text{R}$ do not occur or that ROMe and NH_2Me are formed and immediately redissociated into the original components.

W. R. A.

Chlorine-induced decomposition of diethyl ether [and of acetaldehyde]. H. P. MEISSNER and H. J. SCHUMACHER (Z. physikal. Chem., 1940, 185, 447–464).—The decomp. of Et_2O at 400° under the influence of Cl_2 has been studied. All the free Cl_2 disappears instantaneously, but the decomp. continues. The same is true of a decomp. of MeCHO induced by Cl_2 . Moreover, the products of either decomp. are able to induce the decomp. of fresh portions of Et_2O . The first, very rapid, stages are $\text{Et}_2\text{O} + \text{Cl}_2 = \text{MeCHO} + \text{EtCl} + \text{HCl}$ and $\text{MeCHO} + \text{Cl}_2 = \text{MeCl} + \text{HCl} + \text{CO}$. At the same time small amounts of a substance are formed which catalyses the decomp. of the excess of Et_2O , MeCHO , and EtCl . This catalyst is volatile between -140° and -110° , but no known substance which might be present and is volatile in this range has the observed catalytic power.

F. J. G.

Interaction of di- β -chloroethyl ether with ethylenediamine. M. E. HULTQUIST and E. H. NORTHEY (J. Amer. Chem. Soc., 1940, 62, 447–448).— $(\text{Cl}[\text{CH}_2]_2\text{O})$ with an excess of $(\text{CH}_2\text{NH}_2)_2$ gives 4- β -aminomorpholine (58%) with some ethylenedi-4-morpholine, m.p. 70–73°, b.p. 164–166°/30 mm. (*dihydrochloride*, decomp. and sublimates at $>250^\circ$), and $(\text{NH}_2[\text{CH}_2]_2\text{NH}[\text{CH}_2]_2)_2\text{O}$, b.p. 200–203°/30 mm. (*tetrahydrochloride*, m.p. 185–187°).

R. S. C.

Preparation of $\alpha\gamma$ -epoxides. R. LESPIEAU (Bull. Soc. chim., 1940, [v], 7, 254–258).— $\text{Cl}[\text{CH}_2]_2\text{CHO}$ (prep. from $\text{CH}_2\text{:CH}\cdot\text{CHO}$ described) is transformed by MgEtBr into $\text{Cl}[\text{CH}_2]_2\text{CH}\cdot\text{OH}$, the acetate, b.p. 81°/13 mm., of which is converted by KOH at 140–170° into $\alpha\gamma$ -oxido-*n*-pentane, b.p. 88.5–89°/748 mm. Treatment of $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ with HCl gives trimeric β -chlorobutaldehyde, b.p. 192°/14 mm.; under specified conditions a partly monomeric form is obtained, which is transformed by MgEtBr into β -chloro-*n*-heptan- δ -ol, b.p. 75°/15 mm. The corresponding acetate, b.p. 83–84°/11 mm., is converted by KOH mainly into Δ^8 -hepten- δ -ol, b.p. 133–135°, which freely absorbs Br .

H. W.

Preparation of ethers of chlorohydrins. I. V. A. SKLJAROV (J. Gen. Chem. Russ., 1939, 9, 2121–2125).— $\text{Ph}\cdot\text{SO}_2\cdot\text{NCl}_2$ reacts with alcohol-olefine mixtures: $\text{Ph}\cdot\text{SO}_2\cdot\text{NCl}_2 + 2\text{ROH} \rightarrow \text{Ph}\cdot\text{SO}_2\cdot\text{NH}_2 + 2\text{ROCl}$; $\text{ROCl} + \text{CH}_2\cdot\text{CR}'_2 \rightarrow \text{CH}_2\text{Cl}\cdot\text{CR}'_2\cdot\text{OR}$ ($\text{R}' = \text{H}$, $\text{R} = \text{Me}$, Et , Pr , b.p. 119–120°, Bu , b.p. 139–141°; $\text{R}' = \text{Me}$, $\text{R} = \text{Me}$, b.p. 117–119°, Et , b.p. 125–126°, Pr^a , b.p. 137°, Pr^i , b.p. 150–151°, Bu^a , b.p. 160°). With $\text{CH}_2\cdot\text{CHMe}$ the isomeric ethers

$\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{OR}$ ($\text{R} = \text{Me, Et, Pr}^a$, b.p. 129—130°) and $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{OR}$ ($\text{R} = \text{Me, Et, Pr}^a$) are obtained.

R. T.

Synthesis of β -bromo-ethers by the bromoamide method. I. Reaction of alcohols with benzenesulphondibromoamide in presence of olefines. M. V. LICHOSCHERSTOV, R. A. ARCHANGELSKAJA, and T. V. SCHALAEVA (J. Gen. Chem. Russ., 1939, 9, 2085—2096).— $(\text{CHMe})_2$ in ROH at -15° and $\text{Ph}\cdot\text{SO}_2\cdot\text{NBr}_2$ give ethers $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{OR}$ ($\text{R} = \text{Me}$, b.p. 64—65°/55 mm.; $\text{R} = \text{Et}$, b.p. 72—73°/25 mm.; $\text{R} = \text{Bu}^a$, b.p. 86.5—88°/25 mm.; $\text{R} = \text{Bu}^b$, b.p. 82.5—83°/25 mm.; $\text{R} = \text{isoamyl}$, b.p. 97—98.5°/25 mm.). $\text{CH}_2\cdot\text{CHEt}$ in EtOH similarly yields a mixture of $\text{CH}_2\text{Br}\cdot\text{CHEt}\cdot\text{OEt}$ and $\text{CHEtBr}\cdot\text{CH}_2\cdot\text{OEt}$. Two diastereoisomerides of β -bromo- γ -benzenesulphonamidobutane, m.p. 86.5° and 108°, are obtained as by-products of the reaction; they are converted by KOH into *trans*-, m.p. 77°, and *cis*-dimethyl-*N*-benzenesulphonylethyleneimine.

R. T.

Catalytic action of toluene-*p*-sulphonic acid in the reaction of acetals with pentaerythritol. V. G. MCHITARIAN (J. Gen. Chem. Russ., 1939, 9, 1923—1925).—The following substances were obtained by condensing pentaerythritol with acetals, in presence of traces of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$: *pentaerythritol di-n-butaldehyde acetal*, m.p. 50—60.5°, *diisovaleraldehyde acetal*, m.p. 110—112°, *dichloroacetal*, m.p. 91.8°, and *dicyclohexanone ketal*.

R. T.

Synthesis of α - and β -glycerophosphoric acid. Y. OBATA (J. Agric. Chem. Soc. Japan, 1940, 16, 175—180).— α -*iso*Propyleneglycerol is converted by POCl_3 followed by hydrolysis and treatment with $\text{Ba}(\text{OH})_2$ into Ba α -glycerophosphate, whilst Ba β -glycerophosphate is similarly obtained from α -*benzylideneglycerol*. The separation of the two acids and formation of the insol. double Ba salt with $\text{Ba}(\text{NO}_3)_2$ in the case of the β -acid (Karrer *et al.*, A., 1926, 384) is confirmed.

J. N. A.

Thiomethylene radical. II. Behaviour with chlorine and water. S. W. LEE and G. DOUGHERTY (J. Org. Chem., 1940, 5, 81—85).— RSO_2Cl are obtained in good yield from $\text{CH}_2(\text{SR})_2$ (I) ($\text{R} = \text{Et, Bu}^a, n\text{-C}_5\text{H}_{11}, \text{CH}_2\text{Ph}$), R_2S ($\text{R} = \text{Bu}^a, \text{CH}_2\text{Ph}$), or R_2S_2 ($\text{R} = \text{Et, } n\text{-C}_5\text{H}_{11}, \text{CH}_2\text{Ph}$) with excess of Cl_2 in aq. AcOH (sometimes saturated with HCl) at room temp. Similarly, $\text{CMe}_2(\text{SEt})_2$ gives EtSO_2Cl and Cl-derivatives of COMe_2 ; Bu^a_2SO affords $\text{Bu}^a\text{SO}_2\text{Cl}$; Bu_2SO_2 and sulphonol are unaffected. Fission may occur after oxidation to the sulfoxide. The reaction with (I) is: $\text{CH}_2(\text{SR})_2 + 6\text{Cl}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{RSO}_2\text{Cl} + \text{CH}_2\text{O} + 10\text{HCl}$; intermediate stages appear to be: $\text{CH}_2(\text{SR})_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{R}_2\text{S}_2 + \text{CH}_2\text{O} + 2\text{HCl}$ and $\text{R}_2\text{S}_2 + 2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{R}_2\text{S}_2\text{O}_2 + 4\text{HCl}$ (proved for the CH_2Ph compound). Trithian reacts thus: $(\text{CH}_2\text{S})_3 + 7\text{Cl}_2 + 5\text{H}_2\text{O} \rightarrow 2\text{CH}_2\text{Cl}\cdot\text{SO}_2\text{Cl} + \text{CH}_2\text{O} + 10\text{HCl} + \text{S}$.

H. B.

Synthesis of sodium tetradecanedisulphonate. G. C. H. STONE (J. Amer. Chem. Soc., 1940, 62, 571—572).—*Tetradecamethylene dibromide* (prep. from the glycol by HBr), b.p. 172—175°/2—3 mm., and K Et xanthate in boiling EtOH give a liquid dixanthate,

converted by $\text{Br}\cdot\text{H}_2\text{O}$ etc. into Na_2 *tetradecane- α , ϵ -disulphonate*.

R. S. C.

Fluorination. Antimony fluoride as a fluorinating agent. S. A. VOZNESENSKI (J. Gen. Chem. Russ., 1939, 9, 2148—2152).— SbF_3 in C_6H_6 added to AcCl gives AcF in 30% yield. BzF is obtained similarly in 77% yield, with some $\text{C}_6\text{H}_4\text{Bz}\cdot\text{COF}$ as a by-product.

R. T.

Preparation of esters. VII. N. M. ABRAMOVA and B. N. DOLGOV (J. Gen. Chem. Russ., 1939, 9, 1976—1982).— $\text{MeCHO}\cdot\text{H}_2$ mixtures are passed over Cu-U or Cu-Al catalyst at 275°; the product consists of EtOAc 62, EtOH 36, MeCHO 1.2, and AcOH 0.4%; EtOH- H_2 mixtures give a condensate containing EtOAc 33 and MeCHO 30% in these conditions. The yield of AcOH and MeCHO falls, and of EtOAc and EtOH rises, with increasing $[\text{H}_2]$ of the vapour. Similar results are obtained with PrCHO . The method is probably general.

R. T.

Synthesis of acetates of higher alcohols by their catalytic dehydration.—See B., 1940, 264.

Reaction of halogenoamides with acids in presence of olefines. I. Synthesis of esters of chlorohydrins of isomeric butenes. II. Reaction of benzenesulphondibromoamide with acids in presence of Δ^2 -butene. M. V. LICHOSCHERSTOV and A. A. PETROV (J. Gen. Chem. Russ., 1939, 9, 2000—2008, 2012—2016).—I. $(\text{CHMe})_2$ (I), org. acids, and $\text{PhSO}_2\cdot\text{NCl}_2$ (II) in Et_2O react at -5° as follows: (II) + $\text{RCO}_2\text{H} \rightarrow \text{PhSO}_2\cdot\text{NHCl}$ (III) + $\text{R}\cdot\text{CO}_2\text{Cl}$ (IV); (III) + (I) $\rightarrow \text{Cl}\cdot[\text{CHMe}]_2\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$; (IV) + (I) $\rightarrow \text{R}\cdot\text{CO}_2\cdot[\text{CHMe}]_2\cdot\text{Cl}$ ($\text{R} = \text{H}$, b.p. 147—149°; $\text{R} = \text{Me}$, b.p. 161—165°; $\text{R} = \text{CH}_2\text{Cl}$, b.p. 212—214°; $\text{R} = \text{CCl}_3$, b.p. 124.5°/3 mm.). $\text{CH}_2\cdot\text{CMe}_2$, org. acids, and $\text{NH}_2\cdot\text{CO}\cdot\text{NCl}_2$ (24 hr. at room temp.) give $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$ and $\text{R}\cdot\text{CO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$ ($\text{R} = \text{H}$, b.p. 144.5—146°; $\text{R} = \text{Me}$, b.p. 153—154.5°; $\text{R} = \text{CH}_2\text{Cl}$, b.p. 102—105°/30 mm.; $\text{R} = \text{CCl}_3$, b.p. 117—119°/30 mm.).

II. (I), org. acids, and $\text{PhSO}_2\cdot\text{NBr}_2$ in Et_2O at -15° react as follows: $\text{PhSO}_2\cdot\text{NBr}_2 + 2(\text{I}) + 2\text{R}\cdot\text{CO}_2\text{H} \rightarrow 2\text{R}\cdot\text{CO}_2\cdot[\text{CHMe}]_2\cdot\text{Br} + \text{PhSO}_2\cdot\text{NH}_2$ [$\text{R} = \text{H}$, b.p. 53.5—56°; $\text{R} = \text{Me}$, b.p. 62.5—64.5°; $\text{R} = \text{CH}_2\text{Cl}$, b.p. 106.5—107°; $\text{R} = \text{CCl}_3$, b.p. 117—117.5°; $\text{R} = \text{Pr}$, b.p. 88—89°; $\text{R} = \text{Bu}^b$, b.p. 95.5—97° (all b.p. at 10 mm.)].

R. T.

Use of mercuric acetate in organic preparations. II. Use as an oxidising agent. N. V. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1940, 11, A, 23—27; cf. A., 1939, II, 496).—The progress of oxidation reactions using $\text{Hg}(\text{OAc})_2$ as oxidising agent cannot be followed by weighing the amount of HgOAc pptd. from time to time since there are complications due to the oxidation of the solvent induced by the presence of the substance to be oxidised. Most compounds containing $>\text{CH}\cdot\text{OH}$ produce HgOAc in MeOH. Convenient methods for the prep. of pure benzil, quinhydrone, and HgOAc are described.

W. R. A.

Relationships between polyvinyl acetates and alcohols. W. H. McDOWELL and W. O. KENYON (J. Amer. Chem. Soc., 1940, 62, 415—417).—Hydrolysis of polyvinyl acetates (mol. wt. 16,500—69,200),

prepared in the laboratory, gives alcohols of lower mol. wt., no further change occurring on reacylation or (one example only) on repeating the cycle. With commercial samples (mol. wt. 6900—73,700) degradation occurs mainly during reacylation and very little during hydrolysis. Degradation may be due to rupture of unstable linkings, possibly including O derived from the peroxide catalyst. R. S. C.

Cleavage of unsaturated fatty acids. D. PRICE and R. GRIFFITH (J. Amer. Chem. Soc., 1940, 62, 450—451).—The work of Hsing and Chang (A., 1940, II, 65) was anticipated by Nunn *et al.* (A., 1935, 54) and others. R. S. C.

Introduction of substituted vinyl groups. V. Rearrangement involving migration of an allyl group in a three-carbon system. A. C. COPE and (Miss) E. M. HARDY (J. Amer. Chem. Soc., 1939, 62, 441—444; cf. adjoining abstract).—CMeEt:C(CN):CO₂Et (I), CH₃:CH:CH₂Br, and NaOEt-EtOH give *Et* α -cyano- β -methyl- α -allyl- Δ^{β} -n-pentenoate (II) (34%), b.p. 94.5—96°/1 mm. The structure of (II) is proved by hydrogenation (Pd-C; EtOH) to *Et* α -cyano- β -methyl- α -n-propyl-n-valerate (III), b.p. 122.5—123.5°/11 mm., and conversion thereof by CO(NH₂)₂-NaOEt-EtOH etc. into 5-n-propyl-5-sec-butylbarbituric acid, m.p. 135—137°. (III) is also obtained by hydrogenating (Pd-C; EtOH; 1—2 atm.) (I) to CHMeEt:CH(CN):CO₂Et, b.p. 105—106°/11 mm., and condensing this with PrⁿBr-NaOEt-EtOH. Heating at 150—160° (4 hr.) or 260° (20 min.) rearranges (II) to *Et* α -cyano- β -methyl- γ -allyl- Δ^{α} -n-pentenoate, b.p. 147—148°/16 mm., the structure of which is proved by the exaltation (+1.53) of $[M]_D$, cleavage by conc. aq. NH₃ at room temp. to CN:CH₂:CO:NH₂ and COEt:CH₂:CH:CH₂ (IV), b.p. 137—138° (semicarbazone, m.p. 84—85°; 2:4-dinitrophenylhydrazones, m.p. 41—42°), and synthesis from (IV), CN:CH₂:CO₂Et, and NH₄OAc in C₆H₆-AcOH. Compounds in which the allyl of (II) is replaced by Me, Pr, or Bu do not rearrange. A cyclic rearrangement mechanism is probable. R. S. C.

Manufacture of higher fatty acid chlorides.—See B., 1940, 191.

Selective hydrogenation under reduced pressure of olive oil and its fatty acids. R. ESCOURROU and P. SAUARY (Bull. Soc. chim., 1940, [v], 7, 180—184).—Hydrogenation (Raney Ni) of olive oil and of the fatty acids therefrom at 180° (and 95°) shows marked selectivity if the pressure is sufficiently low. H. W.

Petroselic acid. G. FIGULEVSKI and N. SIMONOVA (J. Gen. Chem. Russ., 1939, 9, 1928—1932).—Petroselic acid (I) and H₂SO₄ (20 hr. at 0°) yield ζ -hydroxystearic acid, m.p. 81.5—82° (Ba, m.p. 155°, and Ca, m.p. 130—131°, salts; *Et* ester, m.p. 37.5°). HBr and a solution of (I) in AcOH, at room temp., yield ζ -bromostearic acid, m.p. 49.5—50.5°, which when treated with KOH in EtOH gives the elaidic form of (I), from which the oxide of Δ^{α} -octadecenoic acid is obtained by oxidation with AcO₂H. R. T.

Alkaloids of *Heliotropium lasiocarpum*. Structure of heliotropic acid. G. P. MENSCHIKOV

(J. Gen. Chem. Russ., 1939, 9, 1851—1855).—Heliotropic acid (I) heated with PbO₂ in 5% H₃PO₄ yields α -methoxyethyl *Pr*ⁿ ketone, b.p. 144—146°, $[\alpha]_D^{25} +22.5^\circ$ (semicarbazone, m.p. 146—147°; oxime, b.p. 108.5—109.5°/16 mm.), which with MgPhBr gives β -methoxy- γ -phenyl- δ -methylpentan- γ -ol, b.p. 112—113°/11 mm., $[\alpha]_D^{25} +17.5^\circ$, oxidised by CrO₃ to CPhPrⁿ. (I) is therefore β -methoxy- δ -methylpentan- γ -ol- γ -carboxylic acid. R. T.

Copolymerisation of maleic polyesters.—See B., 1940, 223.

Introduction of substituted vinyl groups. IV. Primary α -alkenylalkylmalonic esters. A. C. COPE, W. H. HARTUNG, E. M. HANCOCK, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1940, 62, 314—316; cf. A., 1939, II, 48).—Prep. of CHR:CH:CR'(CO₂Et)₂ (A) from CHR:CH:CN(CO₂Et)₂ and R'Br or R'I fails if R = H, but succeeds when R = alkyl if (A) is added to NaOEt-EtOH at -5° to -10°, treated with R'Hal, and immediately heated to the b.p. Yields increase (max. 95%) as R increases in mol. wt. The following are described. *Et*₂ α -n-, b.p. 138—140°/20 mm., and α -iso-propyl- Δ^{β} -n-butene- $\alpha\alpha$ -dicarboxylate, b.p. 135—135.5°/19 mm., *Et*₂ α -propenyl-n-pentane- $\alpha\alpha$ -dicarboxylate, b.p. 148—151°/20 mm., *Et*₂ α -ethyl-, b.p. 134—135°/18 mm., α -n-, b.p. 142—145°/19 mm., and α -iso-propyl-, b.p. 141—143°/19 mm., α -allyl-, b.p. 144—145°/17 mm., α -n-, b.p. 152—156°/19 mm., and α -sec-butyl-, b.p. 159—160°/28 mm., and $\alpha\delta$ -dimethyl-, b.p. 119—122°/9 mm., Δ^{β} -n-pentene- $\alpha\alpha$ -dicarboxylate. *Et*₂ γ -methyl- α -ethyl- Δ^{β} -butene- $\alpha\alpha$ -dicarboxylate, b.p. 140—141°/24 mm. *Et*₂ α -ethyl-, b.p. 154—157°/27 mm., α -n-, b.p. 161—163°/26 mm., and α -iso-propyl-, b.p. 160—163°/28 mm., Δ^{β} -n-hexene- $\alpha\alpha$ -dicarboxylate. *Et*₂ δ -methyl- α -ethyl-, b.p. 141—142°/19 mm., α -n-, b.p. 154—156°/26 mm., and α -iso-propyl-, b.p. 152—153.5°/26 mm., Δ^{β} -n-pentene- $\alpha\alpha$ -dicarboxylate. *Et*₂ α -methyl-, b.p. 164—166°/27 mm., and α -ethyl- Δ^{β} -n-heptene- $\alpha\alpha$ -dicarboxylate, b.p. 168—169.5°/28 mm. R. S. C.

mesoMethyltetradecylsuccinic acid. M. ASANO and T. AZUMI (J. Pharm. Soc. Japan, 1939, 59, 214—216).—CHMe(CO₂Et)₂, NaOEt, and Et α -bromopalmitate in EtOH at 130—140° give *Et*₂ heptadecane- $\beta\gamma\gamma$ -tricarboxylate, b.p. 220—230°/4 mm., hydrolysed to the tricarboxylic acid, decomp. 127°, which is decarboxylated at 130—140° to anti- α -methyl- α' -tetradecylsuccinic acid, m.p. 98—101°, isomeric with the acid of Asano *et al.* (A., 1935, 65). H. W.

Formation of boro-diol complexes. Y. TSUZUKI and Y. KIMURA (Bull. Chem. Soc. Japan, 1940, 15, 27—31; cf. A., 1938, I, 354).—H₃BO₃ does not react with *Et*₂ *d*-tartrate, but BO₂⁻ forms a *l*-cyclic boro-diol complex, formation of which increases with increasing [BO₂⁻] and with decreasing temp. D. F. R.

Condensation of ethylene oxides with malonic ester. K. G. PACKENDORFF (Compt. rend. Acad. Sci. U.R.S.S., 1939, 25, 387—391).—Excess of (CH₂)₂O and CH₂(CO₂Et)₂ with piperidine or NHMe₂ at room temp. for 10 days give $\alpha\alpha$ -dihydroxypentane- $\gamma\gamma$ -dicarboxylolactone, m.p. 110° (85% yield) (cf. bis- γ -butyro-

lactone- α -spiran of Leuchs *et al.*, A., 1912, i, 714). At 80—120° yields are less. A. T. P.

Action of halogen halides on α -dihydroxypentane- γ -dicarboxylodilactone. K. G. PACKENBORFF (Compt. rend. Acad. Sci. U.R.S.S., 1939, 25, 392—393; cf. preceding abstract).—The dilactone and HCl at 140°, or refluxing with HBr or HI, give α -(β' -chloro-, b.p. 156—157°/28 mm., -bromo-, b.p. 168—169°/25 mm., or -iodo-ethyl)butyrolactone, b.p. 178—180°/25 mm., 154°/5 mm., respectively.

A. T. P.

Syntheses and properties of compounds of the type $\text{CH}_2[\text{CH}(\text{COR})_2]_2$ (R = OEt or Me). M. RENARD (Bull. Acad. roy. Belg., 1939, [v], 25, 401—415).— Et_4 methylenedimalonate [Et_4 propane- $\alpha\gamma\gamma$ -tetracarboxylate] (I), b.p. 195°/8 mm., m.p. -30°, is obtained from $\text{CH}_2\text{Cl}\cdot\text{OMe}$ and $\text{CHNa}(\text{CO}_2\text{Et})_2$ followed by very slow distillation of the product, the reactions being $\text{CH}_2\text{Cl}\cdot\text{OMe} + \text{CHNa}(\text{CO}_2\text{Et})_2 \rightarrow \text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ (II); (II) + $\text{CH}_2(\text{CO}_2\text{Et})_2 \rightarrow$ (I) + MeOH. Alternatively, $\text{CH}_2(\text{CO}_2\text{Et})_2$ is brought into reaction with Mg activated by I and CH_2Br_2 and the product is treated with $\text{CH}_2\text{Cl}\cdot\text{OMe}$. Rapid distillation of the product obtained from $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ and $\text{CH}_2\text{Cl}\cdot\text{OMe}$ leads mainly to Et β -methoxymethoxycrotonate, whereas by slow distillation Et_2 methylenediacetoacetate, b.p. 182—183°/13 mm., is obtained in 64% yield; resinous products are frequently formed if the Cu derivative is used. CH_2Ac_2 is converted into its dry Na derivative, which is transformed by $\text{CH}_2\text{Cl}\cdot\text{OMe}$ in dry Et_2O into methylenediacetylacetone (III), b.p. 160—165°/10 mm.; this passes slowly when kept, more rapidly when treated with 10% H_2SO_4 , into diacetyl-*m*-cresol, m.p. 109—110°, also obtained with Cu_2O when (III) is treated with $\text{Cu}(\text{OAc})_2$. Vals. of *n* and *d* are recorded. The reactions may be represented: $\text{NaR} + \text{CH}_2\text{Cl}\cdot\text{OMe} \rightarrow \text{CH}_2\text{R}\cdot\text{OMe}$ (III) + NaCl and (IV) + HR \rightarrow CH_2R_2 + MeOH (V). The second change is easily realised separately, but for its incidence in this system it is necessary that NaR should be converted into HR. This is possible since $\text{CH}_2\text{Cl}\cdot\text{OMe}$ contains HCl and on distillation gives a mixture of max. b.p. containing rather more free HCl than is necessary to convert half the NaR present into HR and NaCl. A part of the metallic derivative is therefore converted into HR and the remainder reacts normally with $\text{CH}_2\text{Cl}\cdot\text{OMe}$ to give the $\cdot\text{CH}_2\cdot\text{OMe}$ derivative. If the starting point is the Na derivative the change (V) proceeds slowly and the amount of CH_2R_2 produced is then a function of the rate of distillation, whereas if the Cu compound is used the CuCl formed has a catalytic action whereby all the $\cdot\text{CH}_2\cdot\text{OMe}$ compound is converted into CH_2R_2 . In confirmation it is observed that the yield of $\text{CH}_2\text{R}\cdot\text{OMe}$ is never >50% of that theoretically possible and that when the Cu derivative of RH is used it is impossible to isolate $\text{CH}_2\text{R}\cdot\text{OMe}$. H. W.

Ferritartrates. E. POULENC-FERRAND (Compt. rend., 1940, 210, 299—301; cf. Pariselle *et al.*, A., 1934, 252).— Na_2CO_3 or K_2CO_3 ppts. alkali ferritartrates when added to a solution of N- FeCl_3 and N-tartaric acid (H_2X) at room temp. The ochre ppt. (I) first formed ($p_H < 3$) gradually dissolves when more carbonate is added and then a brick-red ppt. (II) is

obtained ($p_H < 8$). (I) is $\text{H}_4[\text{Fe}_4\text{X}_3(\text{OH})_4]\cdot 10\text{H}_2\text{O}$ and (II) is K_4 (or Na_4) $[\text{Fe}_4\text{X}_3(\text{OH})_4]$. The following are prepared [R = $\text{Fe}_4\text{X}_3(\text{OH})_4$]: $\text{Na}_2\text{H}_2\text{R}$; $\text{K}_2\text{H}_2\text{R}$; Na_3HR ; K_3HR ; Na_4R ; K_4R . The compounds decompose below 100° and in light. J. L. D.

***dl*-Threonic acid from γ -hydroxycrotonic acid.** J. W. E. GLATTFELD and E. C. LEE (J. Amer. Chem. Soc., 1940, 62, 354—356).—The preps., $\text{CH}_2\cdot\text{CH}\cdot\text{CHO} \rightarrow \text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CN} \rightarrow \text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$ (61%) $\rightarrow \text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (51%) $\rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (I) (27.8%) (cf. Kirmann *et al.*, A., 1932, 600) are modified. $\text{AgClO}_4\text{--OsO}_4$ in H_2O converts (I) into *dl*-threonic acid in 48% (4.1% over-all) yield. R. S. C.

Production of ascorbic acid.—See B., 1940, 244.

Dehydroascorbic acid.—See A., 1940, III, 324.

Isolation of keturonic acids. II. L. T. CREWS, J. P. HART, and M. R. EVERETT (J. Amer. Chem. Soc., 1940, 62, 491—493).—The following are isolated (method: A., 1939, II, 405): *brucine l-xylor*-, + H_2O , m.p. 147—148° (decomp.), $[\alpha]_D^{25} -29.5^\circ$ in H_2O , *l-arabo*-, + $2\text{H}_2\text{O}$, m.p. 160—161°, $[\alpha]_D^{25} -13^\circ$ in H_2O , and *d-chito-keturonate*-, + $1.5\text{H}_2\text{O}$, m.p. 177—178°, $[\alpha]_D^{25} -50.5^\circ$ in H_2O . β -Glucosan gives an anhydride, *keto- β -glucosan*, $\text{C}_6\text{H}_8\text{O}_5$, + $0.5\text{H}_2\text{O}$, m.p. 181—182° (decomp.), $[\alpha]_D^{25} -62^\circ$ in H_2O , slowly hydrolysed by hot 0.6N- H_2SO_4 . A nomenclature for dicarbonyl sugars is suggested. R. S. C.

Detoxication. V. Preparation of *d*-glucurone from ammonium menthylglucuronate. R. T. WILLIAMS (Biochem. J., 1940, 34, 272—275).— NH_4 menthylglucuronate isolated from the urine of rabbits fed with *dl*-menthol is converted into the free acid, which is hydrolysed by boiling 0.4N- H_2SO_4 . 39—40 g. of glucurone are obtained from 100 g. of menthol administered. *Glucuronic acid 2:4-dinitrophenylhydrazide* has m.p. 205° (decomp.).

J. N. A.

So-called artificial humic acids. I. UBALDINI and C. SINRAMED (Atti X Congr. Internaz. Chim., 1938, III, 682—689).—Sucrose or glucose in conc. HCl gives products (I) resembling humic acids (cf. Plungian *et al.*, A., 1935, 623). Similar products (II) are obtained from *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ and pyrogallol with $\text{K}_2\text{S}_2\text{O}_8$ (cf. Eller *et al.*, A., 1920, i, 733). (II) are sol. in dil. alkali, but (I) are sol. only to a very small extent. The C content of (I) is > that of (II). The total acidity of (I) is < that of humic acids (III) from lignite or peat < that of (II). Content of CO_2H and phenolic OH is also recorded. (I) and (II) do not very closely resemble either (III) (which always contain N) or one another.

E. W. W.

Structure of pectin substances. T. K. GAPONENKO (J. Gen. Chem. Russ., 1939, 9, 1752—1754).—Polygalacturonic acid from sugar beet has a polymerisation coeff. of 165; that of its NO_2 -derivative is 75. R. T.

Catalytic action of vanadium oxides in conversion of methyl alcohol into formaldehyde.—See B., 1940, 190.

Free radicals in the pyrolysis of acetaldehyde. M. BURTON, J. E. RICCI, and Y. W. DAVIS (J. Amer. Chem. Soc., 1940, 62, 265—267).—The formation of free alkyl radicals in low concn. from the pyrolysis of MeCHO at 500° has been demonstrated by their power of transporting Ra-D (Pb) mirrors, using a modification of the apparatus of Leighton and Mortensen (A., 1936, 573). W. R. A.

Manufacture of α -chloro- β -alkoxybutaldehydes.—See B., 1940, 191.

Anomalies in the $\alpha\beta$ -unsaturated aldehyde and ketone series. V. I. ESAFOV (J. Gen. Chem. Russ., 1939, 9, 1841—1845).—Polemical (cf. Tschelincev, A., 1936, 996). R. T.

Improved apparatus for the laboratory preparation of keten and butadiene. J. W. WILLIAMS and C. D. HURD (J. Org. Chem., 1940, 5, 122—125).—A lamp (containing an electrically-heated, coiled "Chromel A" filament) capable of converting COMe₂ into keten (0.45 mol. per hr.) and cyclohexene into (CH₂:CH)₂ (0.28 mol. per hr.) is described. H. B.

Oxidation of organic compounds with selenium dioxide. VI. **Oxidation of ketones in alcoholic solutions.** N. N. MELNIKOV and M. S. ROKITZKAJA (J. Gen. Chem. Russ., 1939, 9, 1808—1812).—The velocity of oxidation of ketones by SeO₂ in alcoholic solutions at 30° varies as follows: COMe₂ > COMeEt > COMePr; MeOH < EtOH < BuOH < BuⁱOH > iso-C₅H₁₁OH; aq. alcohols > anhyd. alcohols. R. T.

Preparation of aliphatic α -ketols from magnesium organic compounds and furfuraldehyde. V. I. KUZNETZOV (J. Gen. Chem. Russ., 1939, 9, 2263—2268).—Furfuraldehyde and MgRI in boiling xylene yield compounds OH·CHR·CO·CH₂·CH·CHR [R = Et, b.p. 77—79°/6 mm.; R = Pr^a, b.p. 128—130°/6 mm. (oxime, m.p. 62—63°); R = Bu^β, b.p. 156—158°/5 mm.; R = iso-C₅H₁₁, b.p. 173—175°/6 mm. (oxime, m.p. 106°)], with furyl-ethyl-, propyl-, isobutyl-, b.p. 92—94°/5 mm., or isoamyl-carbinol. R. T.

$\alpha\delta$ -Dibromo- $\alpha\delta$ -dipivalylbutane [$\delta\eta$ -dibromo- $\gamma\theta$ -diketo- $\beta\beta$ -tetramethyl-*n*-decane]. R. C. FUSON and J. W. ROBINSON, jun. (J. Amer. Chem. Soc., 1940, 62, 358—360).—(CH₂·CH₂·COCl)₂ (0.136 mol.) and MgBu^γCl (0.3 mol., optimum) in Et₂O at 0° give $\gamma\theta$ -diketo- $\beta\beta$ -tetramethyl-*n*-decane (I) (25%), m.p. 52—52.5° (di-2:4-dinitrophenylhydrazone, m.p. 251—252°), with ~20% of ϵ -keto- $\zeta\zeta$ -dimethyl-*n*-octoic acid, m.p. 45—47°, b.p. 151—153°/2 mm. (formed by incomplete reaction), and the impure diol (II), (CH₂·CH₂·CHBu^γ·OH)₂, b.p. 119—124°/3.5 mm. An excess of MgBu^γCl gives only an oily reduction product [(II) and/or the derived OH-ketone], from which CrO₃ yields only a little (I). Br-CCl₄ converts (I) into the $\delta\eta$ -Br₂-derivative (III), m.p. 119.5—120°, the structure of which is shown by cleavage of its pyridinium salt by alkali to Bu^γCO₂H. NH₄Et₂ in boiling C₆H₆ converts (III) into $\gamma\theta$ -diketo- $\beta\beta$ -tetramethyl- $\Delta^{\delta\zeta}$ -decadiene (21%), m.p. 145—146° (di-2:4-dinitrophenylhydrazone, m.p. 280—282°), which

does not react with (·CH·CO)₂O, is reduced by Na₂S₂O₄ to a substance, m.p. 70—72°, or by H₂-Raney Ni to (I), and with MgPhBr gives (CHPh·CH₂·COBu^γ)₂. NaCN and (II) in boiling EtOH-EtOAc give $\gamma\theta$ -diketo- $\delta\eta$ -dicyano- $\beta\beta$ -tetramethyl-*n*-decane (IV), m.p. 92—93°, and a liquid cyanocyclobutane or cyanopyran derivative, b.p. 163—168°/6 mm. (2:4-dinitrophenylhydrazone, m.p. 225—227°; oximes, m.p. 183—185° and 146—148°). (IV) liberates 2 CH₄ from MgMeI, but alkylation and ring-closure could not be effected. Hydrolysis of (IV) is difficult, NaOH having no effect and conc. HCl at 140—150° yielding $\gamma\theta$ -dichloro- $\beta\beta$ -tetramethyl-*n*-decane- $\delta\eta$ -dicarboxylamide, m.p. 198—200°. R. S. C.

Photochemical reactions in the *o*-nitrobenzylidene acetals series. XIII. *o*-Nitrobenzylidenexylose and -cyclohexane-1:2-diol. XIV. Constitution of the di-*o*-nitrobenzylidene acetals of glucose, galactose, and mannose and of their products of photochemical isomerisation. XV. Attempted syntheses of disaccharides. L. TANASESCU and M. IONESCU (Bull. Soc. chim, 1940, [v], 7, 77—83, 84—90, 90—94).—XIII (cf. A., 1939, I, 46). Condensation of xylose with *o*-NO₂·C₆H₄·CHO in presence of P₂O₅ at 40—45° gives 1:2:3:5-di-*o*-nitrobenzylidenexylose, m.p. 110—115° (probably a mixture of isomerides), rapidly converted by insolation in CHCl₃ into 1:2-*o*-nitrobenzylidenexylose 3-*o*-nitrosobenzoate, m.p. 130—135°. This is converted by NH₂Ph in glacial AcOH at 100° into 1:2-*o*-nitrobenzylidenexylose *o*-benzeneazobenzoate, m.p. 160—165° after softening, and by BzCl in C₅H₅N into 1:2-*o*-nitrobenzylidenexylose 5-benzoate 3-*o*-nitrosobenzoate, m.p. 85—90°. cycloHexane-1:2-diol and *o*-NO₂·C₆H₄·CHO under the influence of P₂O₅ or, preferably, of H₂SO₄ (1:1 vol.) yield *o*-nitrobenzylidenecyclohexane-1:2-diol (probably a *trans* derivative), m.p. 104—105°. This is isomerised by insolation to 2-hydroxycyclohexyl *o*-nitrosobenzoate, m.p. 145—146° (violent decomp.), which gives green solutions and is converted into 2-hydroxycyclohexyl *o*-benzeneazobenzoate and 2-benzoyloxycyclohexyl *o*-nitrosobenzoate, m.p. 138—142° to a green liquid.

XIV (cf. A., 1936, 593, 1234). Unsuccessful attempts are described to identify the sugar residue of di-*o*-nitrobenzylidene-glucose (I), -galactose (II), and -mannose (III) and of the identical product (IV) obtained by insolation of them. The products of the hydrolysis of (I) by HCl and Pr^aOH are *o*-NO₂·C₆H₄·CHO and minute amounts of a (?) sugar, m.p. 75—77°, which yields a phenylhydrazone, m.p. 120—130° (which does not correspond with any known hexosehydrazone), and an osazone, m.p. 195—198°, which could not be identified. (II) and (III) give different products when hydrolysed but the course of the reaction appears similar. Attempts to oxidise (I), (II), or (III) with conc. HNO₃ lead only to hydrolysis with production of *o*-NO₂·C₆H₄·CHO or *o*-NO₂·C₆H₄·CO₂H according to the duration of the reaction and probable destruction of the sugar component. Since basic acetals are more readily hydrolysed than NO₂-acetals, unsuccessful attempts have been made to condense glucose with *p*-NMe₂·C₆H₄·CHO. (I) and Na₂S₂O₄ in boiling

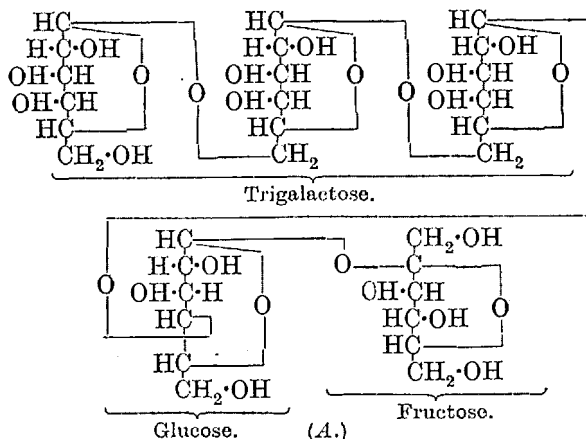
COMe₂-EtOH give a product, m.p. 138—142°, probably a mixture of unchanged (I) and its reduction products. Na₂S in boiling EtOH transforms (I) into a substance giving a phenylhydrazone, m.p. 155—165°; (II) and (III) behave similarly. Reduction could not be effected with Zn dust in EtOH or by H₂ (PtO₂ or spongy Pd in MeOH, EtOAc, or AcOH). Attempted hydrolysis of (IV) gives only ill-defined products. According to conditions (IV) and HNO₃ give very small amounts of an acid, m.p. 130—135°, or a non-acidic compound, m.p. 148—150°, which could not be identified. The same substances result from (IV) whether produced from (I), (II), or (III). Reduction of (IV) with Na₂S gives a material which yields a hydrazone, m.p. 130—140°, which could not be identified.

XV. Attempted condensation of (I), (II), or (III) with acetobromoglucose (V) in presence of Ag₂O gives unchanged material whereas in presence of Hg(OAc)₂ these materials are accompanied by *r-trehalose octaacetate* (VI), m.p. 130° [formed by autocondensation of (V)], deacetylated (NaOMe in MeOH) to *r-trehalose*, m.p. 90°, decomp. 110°, which does not reduce Fehling's solution. If (IV) is treated with Ag₂O in boiling CHCl₃ or dioxan, a substance (VII), m.p. 175°, results. This is also formed by use of Hg(OAc)₂ in boiling dioxan; if (V) is added it is accompanied by (VI). (VII) contains an *o*-NO₂·C₆H₄·CH group since it is transformed by insolation in CHCl₃ into an isomeride, m.p. 180—182°. *o*-Nitrobenzylidenepentaerythrityl *o*-nitrobenzoate and 2-hydroxycyclohexyl *o*-nitrobenzoate are converted by Ag₂O or Hg(OAc)₂ into unidentified compounds.

H. W.

Constitution of verbascode, a new penta-saccharide. S. MURAKAMI (Proc. Imp. Acad. Tokyo, 1940, 16, 12—14; cf. Bourquelot *et al.*, A., 1910, i, 817).—The fresh roots of *Verbascum thapsus* are extracted with hot 95% EtOH and the extract is treated successively with Pb(OAc)₂ and Ba(OH)₂. The Ba compound of verbascode is decomposed by CO₂ and the liberated (I) is purified by pptn. from H₂O by EtOH. (I), m.p. 253°, $[\alpha]_D^{20} +170.2^\circ$, is C₃₀H₅₂O₂₈. It gives the compounds, C₃₀H₃₅O₂₆Ac₁₇, m.p. 132°, $[\alpha]_D^{20} +130.4^\circ$, C₃₀H₃₅O₂₆Bz₁₇, m.p. 132°, $[\alpha]_D^{20} +141.1^\circ$, and C₃₀H₃₅O₂₆(OMe)₁₇, a syrup, $[\alpha]_D^{20} +123.6^\circ$. Hydrolysis of (I) by 20% AcOH gives fructose (II) (1 mol.) and a *tetraose* (III), m.p. 240°, and by dil. H₂SO₄ yields (II) (1 mol.), glucose (IV) (1 mol.), and galactose (3 mols.). Fructosephenylosazone can be isolated after hydrolysis of (I) with yeast- or taka-invertase and galactosephenylmethylhydrazone after hydrolysis with emulsin. The sequence of glycosidic linkings in the mol. of (I) is therefore galactosido-galactosido-galactosido-glucosido-fructose. Exhaustive methylation (Me₂SO₄ and NaOH) of (I) followed by hydrolysis and distillation gives a tetramethylmonose fraction from which 2:3:4:6-tetramethylgalactopyranose (V) is obtained and characterised as the anilide and 1:3:4:6-tetramethylfructofuranose. Further methylation of the trimethylmonose fraction by MeI and Ag₂O gives (V) and 2:3:4:6-tetramethylglucopyranose. The cryst. Me₂ derivative and CPh₃Cl afford 6-triphenylmethyl-2:3:4-trimethylglucose, $[\alpha]_D^{20} +30.9^\circ$. (III) is

oxidised by Br to a mixture of acids from which after exhaustive methylation, hydrolysis, and distillation αβδε-tetramethyl-*d*-gluconic acid is derived, thus showing that the galactose residue is attached to C₄ of (IV). Methylation of (III) followed by hydrolysis and distillation gives a tetramethylmonose fraction and 2:3:4-trimethylgalactopyranose. (I) is therefore (A).



H. W.

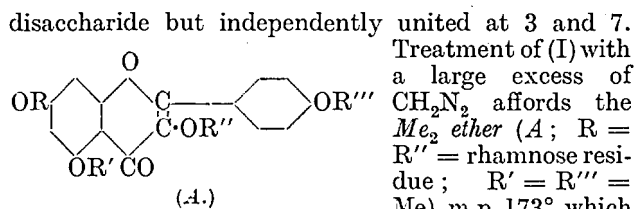
Thermal dissociation of some glucosides. Z. JERZMANOWSKA (Atti X Congr. Internaz. Chim., 1938, III, 212).—Certain glucosides [*e.g.*, quercitrin (I), hyperin, or phloridzin (II)] when acetylated and heated in vac. dissociate into acetylated aglucone and unsaturated anhydro-sugar. Thus (I) gives 2-hydroxyrhamnal triacetate, m.p. 74°. The products from (II) both undergo further change.

E. W. W.

Centaurea scabiosa, L. C. CHARAUX and J. RABATÉ (J. Pharm. Chim., 1940, [ix], 1, 155—162).—Boiling H₂O extracts from the leaves scutellaroside, m.p. ~205°, ~230° (block), $[\alpha]_D^{25} -138^\circ$ in H₂O-C₅H₅N (+2H₂O, $[\alpha]_D^{25} -128^\circ$ in C₅H₅N-H₂O). It gives a green colour with FeCl₃ in EtOH; an alkaline solution is rapidly oxidised and hydrolysis (boiling AcOH-10% H₂SO₄) gives glycuronic acid and scutellarol, m.p. 345—350° (Ac derivative, m.p. 253°), which when fused with KOH affords 1:3:5-C₆H₃(OH)₃ and *p*-OH·C₆H₄·CO₂H.

J. L. D.

Lespedin, a dirhamnoside of campherol. S. HATTORI and M. HASEGAWA (Proc. Imp. Acad. Tokyo, 1940, 16, 9—11).—Lespedin (I) (A; R = R' = rhamnose residue; R' = R'' = H), C₂₇H₃₀O₁₃, from *Lespeza crytobotrya*, forms pale yellow needles or plates, m.p. 234° (+3.5H₂O). In EtOH it gives a violet-brown colour with FeCl₃. It is hydrolysed by boiling, dil. mineral acids to campherol (1 mol.) and *l*-rhamnose (II) (2 mols.). (I) separates from H₂O in thin prisms, m.p. 193° (indef.); since the m.p. is unchanged after 3 hr. at 110°, (I) is probably dimorphous. Its identity with campheritrin from the leaves of *Indigofera arrecta* is doubtful. (I) is transformed by CH₂N₂ in MeOH into the *Me ether* (A; R = R' = rhamnose residue; R' = H; R'' = Me), m.p. 236°, which gives a violet-brown colour with FeCl₃ and is hydrolysed to campherol Me ether. The two mols. of (II) are not therefore present as a



Treatment of (I) with a large excess of CH_2N_2 affords the Me_2 ether (A; $\text{R} = \text{R}'' = \text{rhamnose residue}$; $\text{R}' = \text{R}''' = \text{Me}$), m.p. 173° , which does not develop a colour with FeCl_3 and is hydrolysed to campherol Me_2 ether, which gives a brown-violet reaction with FeCl_3 . Methylation of (I) with MeI and K_2CO_3 in COMe_2 gives the yellow *K* salt of a methylated derivative, converted by dil. HCl into a new glucoside which contains only 1 mol. of (II) and OH additional to those originally present and causative of the violet colour with FeCl_3 . The constitution assigned to (I) is supported by its absorption spectrum.

H. W.

Structure of eisenin.—See A., 1940, III, 367.

Acetolysis of methylated starch. S. PEAT and J. WHETSTONE (J.C.S., 1940, 276—280).—A new method of determining the chain length of starch is described. Trimethylstarch (obtained by exhaustive methylation of potato starch) reacts completely with AcBr in CHCl_3 at 20° in 10 hr. If after a shorter time the mixture is poured on to ice, and the mixed bromohydrins are converted by MeOH into methylglucosides, mixtures of mono-, di-, and tri-saccharides are formed, separable by fractional distillation. After 20 min., the whole of the end group has been removed as tetramethylmethylglucoside (I) [accompanied in the monosaccharide fraction by 2 : 3 : 6-trimethyl- (II) and by some dimethyl-methylglucoside (III)]. The disaccharide fraction (and similarly the tri- and higher fractions) is hydrolysed by MeOH-HCl to (II) and some (III), without (I). The only trimethylmethylglucoside found is (II). After 5 min. only, the whole of the end group is found in (I), in an amount corresponding with a chain length of 27 glucose units.

E. W. W.

Inulin and its mol. wt. S. BEZZI (Atti X Congr. Internaz. Chim., 1938, III, 39—46).—In H_2O , inulin, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ (purification modified), shows cryoscopically a mol. wt. of 3764 ($n = 23$). By isothermal distillation at 20° (cf. Ulmann, A., 1934, 987), a mol. wt. of 7777 ($n = 48$) is found. This is of the same order as that deduced chemically (cf. Haworth *et al.*, A., 1932, 1117), showing that inulin in H_2O is in mol. dispersion. Results obtained by Brintzinger *et al.* (A., 1932, 836) by dialysis are unreliable owing to the thread-like character of the mol. (cf. Staudinger *et al.*, A., 1936, 146). Vals. of K_m obtained viscosimetrically are of the anticipated order of magnitude.

E. W. W.

Natural depolymerisation products of inulin. S. M. STREPKOV (J. Gen. Chem. Russ., 1939, 9, 1990—1999).—A new, non-reducing trifructoside, *polygontin*, sintering at $207\text{—}208^\circ$, $[\alpha]_D^{25} -53.3^\circ$ in H_2O (Ac_{11} derivative, m.p. $84\text{—}85^\circ$, $[\alpha]_D^{25} -38.37^\circ$ in CHCl_3), is isolated from *Polygonatum sewerzowii* roots. It is readily hydrolysed by 1% HCl , but not by invertase, emulsin, or diastase. *Allium sewerzowii* bulbs yield a non-reducing difructoside, *alliuminoside*, m.p. $92\text{—}93^\circ$, $[\alpha]_D^{25} -23.8^\circ$ in H_2O , not hydrolysed by

invertase. *Eremurus sogdianus* roots contain a reducing α -difructoside, *sogdianose*, m.p. $84\text{—}85^\circ$, $[\alpha]_D^{25} -16.4^\circ$ in H_2O (*osazone*, m.p. $198\text{—}199^\circ$), hydrolysed by 1% HCl or invertase, but not by emulsin.

R. T.

Structure of hemicellulose B.—See A., 1940, III, 368.

Glyceryl derivatives of cellulose. S. N. DANILOV, M. E. DINKIN, N. I. ORLOVA, and A. A. RABINKOV (J. Gen. Chem. Russ., 1939, 9, 1674—1681).—Alkali-cellulose and epichlorohydrin yield insol. $\alpha\gamma$ -di-ethers of glycerol, the nitrates and acetates of which are prepared. The $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{C})\cdot$ bridges of these ethers may connect two C of the same or of different $\text{C}_6\text{H}_{10}\text{O}_5$ units. Sol. mono-ethers are obtained with glycide.

R. T.

Reaction of ethylenediamine with carbon disulphide: $\alpha\beta$ -dithiocarbimidoethane. A. J. JAKUBOVITSCH and V. A. KLIMOVA (J. Gen. Chem. Russ., 1939, 9, 1777—1782).— $(\text{CH}_2\cdot\text{NH}_2)_2$ and CS_2 in aq. NaOH (2 hr. at 50°) yield *ethylenebisdithiocarbamic acid* [Na_2 salt, $+6\text{H}_2\text{O}$ (I)], which readily eliminates CS_2 when heated, giving ethylenethiourea. (I) in H_2O and ClCO_2Et at $5\text{—}10^\circ$ afford the substance, $(\text{CH}_2\cdot\text{NH}\cdot\text{CS}_2\cdot\text{CO}_2\text{Et})_2$, m.p. 85.5° (decomp.), which when heated in vac. yields $\alpha\beta$ -dithiocarbimidoethane, b.p. $151.5\text{—}152^\circ/15\text{ mm.}$, $140^\circ/10\text{ mm.}$, and this with NH_2Ph in Et_2O gives $\alpha\beta$ -di(phenylthiocarbamido)ethane, $(\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2)_2$, m.p. $171\text{—}172^\circ$. CS_2 and $(\text{CH}_2\cdot\text{NH}_2)_2$ in EtOH yield the internal salt $\text{S}=\text{CS} > \text{NH}$, the Na salt of which when treated with ClCO_2Et gives the substance $\text{CO}_2\text{Et}\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CS}_2\cdot\text{CO}_2\text{Et}$, m.p. $58\text{—}59^\circ$ (decomp.).

R. T.

Higher ammoniates of complex compounds.—See A., 1940, I, 230.

Structure of amine oxides. I. N-Oxides and NN' -dioxides of tertiary amines. M. POLONOVSKI [with P. BOULANGER and H. TAGHAVI] (Atti X Congr. Internaz. Chim., 1938, III, 303—306).— $(\text{CH}_2\cdot\text{NMe}_3)_2$ (I) gives an N-oxide, $\text{C}_6\text{H}_{16}\text{ON}_2\cdot 4\text{H}_2\text{O}$ (dihydrochloride, m.p. 160° ; dihydrobromide, m.p. 192° ; dipicrate, m.p. 148°). Similarly $\text{NMe}_2\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$ (II) gives an N-oxide ($+ \text{H}_2\text{O}_2$) (hydrochloride, m.p. 179° ; picrate, m.p. 168°). Both these are monobasic to Me-orange. In non-formation of an NN' -dioxide, sparteine (III) resembles (I) and (II), and this property is thus no indication of asymmetry in (III).

E. W. W.

Esters of choline and its homologues. I. S. I. LURIE and Z. I. FEDOROVA (J. Gen. Chem. Russ., 1939, 9, 2075—2080).—Esters of dialkylcholine or its homologues when treated with alkyl halides yield the following quaternary NH_4 salts: γ -dimethylaminopropyl 2-phenylquinoline-4-carboxylate methochloride, m.p. $195\text{—}196^\circ$, and methiodide, m.p. $182\text{—}184^\circ$; γ -diethylaminopropyl 2-phenylquinoline-4-carboxylate ethobromide, m.p. $207\text{—}208^\circ$; β -dimethylaminoethyl 2-phenylquinoline-4-carboxylate methiodide; β -dimethylaminomethyl 2-butoxyquinoline-4-carboxylate methobromide, m.p. $133\text{—}135^\circ$; γ -dimethylaminopropyl 2-butoxyquinoline-4-carboxylate methochloride, m.p. 128

—130°; γ -diethylaminopropyl 2-butoxyquinoline-4-carboxylate ethobromide, m.p. 165—166°; triethyl- β -p-aminobenzoyl ethylammonium bromide, m.p. 159—161°; trimethyl- β -salicyl ethylammonium bromide, m.p. 177—178°; trimethyl- γ -salicylpropylammonium chloride, m.p. 140—142°; triethyl- γ -salicylpropylammonium bromide, m.p. 141—143°. These salts have a physiological action similar to that of choline. R. T.

Synthesis and determination of the lipotropic activity of the betaine hydrochlorides of *dl*-serine, *dl*-threonine, and *dl*-allothreonine. H. E. CARTER and D. B. MELVILLE (J. Biol. Chem., 1940, **133**, 109—116).—Methylation of the NH_2 -acid by KOH-MeOH and hydrolysis of the product by HCl gives *dl*-serine- (I), m.p. 198—199°, *dl*-allothreonine- (II), m.p. 166—168°, and *dl*-threonine-betaine hydrochloride (III), m.p. 162—164°. Hydrolysis of (II) and (III) with NaOH gives MeCHO and betaine. (I), (II), and (III) do not prevent the development of a fatty liver in rats fed on a high-fat, low-protein diet. J. D. R.

Synthesis of β -hydroxyvaline and α -methylamino- β -hydroxy-*n*-butyric acid. M. A. PROKOFIEV and M. M. BOTVINNIK (Compt. rend. Acad. Sci. U.R.S.S., 1939, **25**, 488—492).— $\text{CMe}_2\text{CH}\cdot\text{CO}_2\text{H}$ and $\text{Hg}(\text{OAc})_2$ in MeOH, best (73%) at 18°, give β -methoxy- α -anhydromercuriisovaleric acid,

$\text{OMe}\cdot\text{CMe}_2\cdot\text{CH}\langle\text{Hg}\rangle\text{O}$, m.p. 159—160° (decomp.)

(with ? mixed Hg salts), converted by KBr-Br in H_2O into $\text{OMe}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, which (crude) with 25% aq. NH_3 at 100° gives $\text{OMe}\cdot\text{CMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, new m.p. 253—254° (decomp.), and thence (48% HBr) *dl*-hydroxyvaline (21.6% over-all yield).

$\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ gives similarly α -methylamino- β -hydroxy-*n*-butyric acid, m.p. 234—235° in a sealed tube. R. S. C.

Hydroxyllysine. D. D. VAN SLYKE, A. HILLER, D. A. MACFADYEN, A. B. HASTINGS, and F. W. KLEMPERER (J. Biol. Chem., 1940, **133**, 287—288).—The $(\text{NH}_2)_2$ -acid (I) from gelatin (cf. A., 1938, III, 757) on electrometric micro-titration shows three buffer groups with pK' vals. of 2.20, 8.70, and 9.50 (lysine shows 2.20, 8.90, and 10.28). Oxidation with HIO_4 at p_H 8—12 gives 1 mol. each of NH_3 and CH_2O . From this, with the evidence previously presented (*loc. cit.*), it is suggested that (I) is α -diamino- δ -hydroxy- or α -diamino- ϵ -hydroxy-hexoic acid.

J. D. R.

Alkaline hydrolysis of acetylated dipeptides.—See A., 1940, I, 223.

Sulphonium reactions of methionine and their metabolic significance.—See A., 1940, III, 327.

Condensation of *N*-halogenoamides with aliphatic sulphides. I. V. G. PETROV (J. Gen. Chem. Russ., 1939, **9**, 1635—1641).— NHAcCl and sulphides in anhyd. COMe_2 do not yield the expected sulphinimines. The reaction is $\text{R}_2\text{S} + \text{NHAcCl} \rightarrow \text{R}_2\text{SO} + 2\text{NH}_2\text{Ac}\cdot\text{HCl}$. With chloramine-*B* or -*T* in CHCl_3 , COMe_2 , or aq. EtOH the reactions are: $\text{R}_2\text{S} + \text{R}'\cdot\text{SO}_2\cdot\text{NHCl} \rightarrow \text{R}_2\text{S}\cdot\text{N}\cdot\text{SO}_2\text{R}'$ ($\text{R}' = \text{Ph}$, $\text{R} = \text{Pr}^\beta$, m.p. 98°; $\text{R} = \text{Bu}^\alpha$, m.p. 65°; $\text{R} = \text{isocamyl}$, m.p. 87—88°; $\text{R}' = p\text{-C}_6\text{H}_4\text{Me}$, $\text{R} = \text{Pr}^\beta$, m.p. 101—102; $\text{R} = \text{isocamyl}$, m.p. 112°). R. T.

Action of hydrazine hydrate on derivatives of organic acids. M. FRERI (Atti X Congr. Internaz. Chim., 1938, III, 150—154).—The ester or chloride of dimethylacrylic acid with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (I) gives only resins. Me angelate and (I) in boiling EtOH give dimethylpyrazolone. Tiglyl chloride and (I) in MeOH yield tiglyldihydrazide, m.p. 182—183°. Me tiglate (II) in two experiments gave a small quantity of a substance, m.p. 245°; otherwise (II) or the amide gives only resins. Et *p*-nitrocinnamate and (I) in EtOH give a product, m.p. 147°, containing $2\text{N}_2\text{H}_4$, converted by conc. HCl into a product, m.p. 198°, and into *p*-nitrocinnamhydrazide hydrochloride, m.p. 203°. With anisaldehyde, vanillin, and piperonal, (I) in EtOH gives compounds, $\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}_3$, m.p. 198°, $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3$, m.p. 180°, and $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_3$, m.p. 217°, respectively. Et ethoxycinnamate and (I) in EtOH give a compound, $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2$ (*sic*), m.p. 156°.

E. W. W.

Citracononitrile. G. DUEZ (Bull. Acad. roy. Belg., 1939, [v], **25**, 646—653).—Mesacononitrile (I) is not isomerised by exposure to ultra-violet light in the liquid or gaseous state or in C_6H_6 . In COMe_2 citracononitrile (II), b.p. 106.5—107°/10 mm., m.p. 12.8—13.5°, and an additive product (III) of COMe_2 and (I) or (II) result. The removal of (I) from this mixture is readily effected by fractional distillation whereas (II) and (III) appear to give an azeotropic mixture, b.p. 105—106°/10 mm., which is separated into its components by fractional crystallisation. There is little difference in d but much difference in b.p. and m.p. between (II) and mesacononitrile. The difference in mol. refraction is almost identical with that observed between fumaro- and maleo-nitrile.

H. W.

Attempted preparation of $\alpha\beta$ -oxido- α -ethylpropionitrile. G. JNOFF (Bull. Acad. roy. Belg., 1939, [v], **25**, 632—645).—Addition of HOCl to $\text{CH}_2\text{Cl}\cdot\text{CET}\cdot\text{CN}$ at 0° comparatively rapidly yields (?) α -chloro- α -chloromethylbutyronitrile, b.p. 35—37°/10 mm., $\alpha\beta$ -oxido- α -methylbutyronitrile, b.p. 142.2—142.6°/755 mm. [identical with that obtained by Gerbaux (unpublished work) from angelonitrile and converted by NaOH into $\alpha\beta$ -dihydroxy- α -methylbutyronitrile, m.p. 106.1—106.7°], and β -chloro- α -hydroxy- α -methylbutyronitrile, b.p. 99.5—100.5°/10 mm. $\text{CH}_2\text{Cl}\cdot\text{COEt}$ and KCN readily yield α -hydroxy- α -chloromethylbutyronitrile, b.p. 104.6—104.8°/10 mm., hydrolysed by fuming HCl at 100° to α -hydroxy- α -chloromethyl-*n*-butyric acid, m.p. 85.6—86.4°. Gradual addition of aq. KCN to $\text{CH}_2\text{Cl}\cdot\text{COEt}$ gives a volatile fraction which possibly contains some epoxynitrile and (?) γ -keto- α -propionylhexonitrile, m.p. 29—30° (semicarbazone, m.p. 214—216°), also obtained by the action of KCN on $\text{CH}_2\text{Cl}\cdot\text{CET}(\text{OH})\cdot\text{CN}$. Almost quant. removal of HCN can be effected by 0.1*N*- AgNO_3 from $\text{OH}\cdot\text{CMeEt}\cdot\text{CN}$, $\text{CHMeCl}\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, b.p. 101° or 94°, or $\text{OH}\cdot\text{CET}(\text{CH}_2\text{Cl})\cdot\text{CN}$ whereas $\approx 2\%$ of the HCl is removed. H. W.

Action of ethyl and phenyl azides on fuming sulphuric acid. K. W. SHERK, A. G. HOUPF, and A. W. BROWNE (J. Amer. Chem. Soc., 1940, **62**, 329—331).—When dry PhN_3 vapour is passed slowly into fuming H_2SO_4 at room temp. N_2 is evolved and the

H_2SO_4 becomes maroon colour. After all the gas has been evolved the solution is added to vigorously stirred, ice-cold Et_2O when a bulky, rose-coloured ppt. (I), which is very hygroscopic and becomes blue and sticky on exposure to air, is deposited. It is sol. in H_2O , from which there separate needles, sol. in dil. NaOH , re-pptd. by acid, and giving analysis of 4:1:2: $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (II). (I) chars without melting, yields an aq. solution which gives a positive PhOH test, does not liberate I from acidified KI, but gives a ppt. of BaSO_4 with BaCl_2 and HCl . Analysis and other data indicate that (I) is mainly phenylaminomonopersulphuric-*m*-sulphonic acid which, on hydrolysis, yields (II). Dry EtN_3 vapour passed into fuming H_2SO_4 gives products which are hydrolysed to MeCHO , CH_2O , NH_3 , and NH_2Me . MeCHO and CH_2O are separated by adding excess of conc. aq. NH_3 , which converts CH_2O into $(\text{CH}_2)_6\text{N}_4$ and MeCHO into aldehyde-ammonia, and subsequent distillation. The absence of NH_2OH indicates that ethylaminomonopersulphuric acid is not first formed. Mechanisms for the reactions are advanced.

W. R. A.

Action of diazomethane on zinc chloride [in ether]. G. CARONNA and B. SANSONE (Atti X Congr. Internaz. Chim., 1938, III, 77—81).— ZnCl_2 in Et_2O reacts rapidly with CH_2N_2 , forming ZnO , N_2 , $n\text{-C}_4\text{H}_{10}$, and $(\text{CH}_2\text{Cl})_2$ (identified by conversion by $\text{Ag}_2\text{O}\cdot\text{H}_2\text{O}$ into glycol and thence into $\text{H}_2\text{C}_2\text{O}_4$), by way, it is suggested, of an intermediate compound, $\text{Zn}(\text{CH}_2\text{Cl})_2$.

E. W. W.

Reaction of silicon tetrachloride with esters. J. N. VOLNOV (J. Gen. Chem. Russ., 1939, 9, 2269—2282).— SiCl_4 and EtOAc (4 days at the b.p.) yield $\text{Si}(\text{OAc})_4$ (I), EtCl , $\text{SiCl}_3(\text{OEt})_2$, and AcCl . With Pr^nOAc the products are (I) and PrCl . Bu^nOAc gives (I) and AcCl , $\text{CH}_2\text{Bu}^n\text{OAc}$ gives AcCl and *dichlorodiisomayloxymonosilan*, b.p. 108—110°, $\text{CH}_2\text{Ph}\cdot\text{OAc}$ affords AcCl , CH_2PhCl , and SiO_2 , $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{OAc}$ yields AcCl , $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Cl}$, and SiO_2 , PhOAc gives AcCl , $\text{SiCl}_3\cdot\text{OPh}$, $\text{SiCl}_2(\text{OPh})_2$, $\text{SiCl}(\text{OPh})_3$, and $\text{Si}(\text{OPh})_4$, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OAc}$ yields AcCl and $\text{Si}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{p})_4$.

R. T.

Electrolysis of higher aliphatic organomagnesium halides in diethyl ether. W. V. EVANS, D. BRAITHWAITE, and E. FIELD (J. Amer. Chem. Soc., 1940, 62, 534—536).—The amount of R_2 formed by electrolysis of MgRHal in Et_2O increases with the mol. wt. of R and the straightness of the chain. MgBu^nBr gives ~100% (>85%) of Bu^n_2 . MgBu^iBr gives ~96% of Bu^i_2 . $\text{CHMeEt}\cdot\text{MgBr}$ gives ~100% of $(\text{CHMeEt})_2$. MgBu^nBr gives mainly *iso*- C_4H_8 and $\text{-C}_4\text{H}_{10}$. *n*- $\text{C}_6\text{H}_{13}\cdot\text{MgBr}$ gives ~100% (>82.5%) of $n\text{-C}_{12}\text{H}_{26}$.

R. S. C.

Organo-aluminium compounds. I. Preparation. A. V. GROSSE and J. M. MAVITY (J. Org. Chem., 1940, 5, 106—121).—The reaction, $2\text{Al} + 3\text{RX} \rightarrow \text{AlRX}_2 + \text{AlR}_3\text{X}$, is successfully applied to MeCl , EtCl , MeBr , EtBr , MeI , EtI , Pr^nI , PhI , and *p*- $\text{C}_6\text{H}_4\text{MeI}$; the RX is added, with stirring, to Al (preferably turnings) in presence of N_2 and a catalyst [I; Al halide; Al alkyl or aryl halide; little Et_2O (for ArI; generally avoided)]. Satisfactory separation of AlMeCl_2 and AlMe_2Cl is effected by a single vac.

fractionation (Podbielniak), but disproportionation (during distillation) occurs with AlMeBr_2 and AlMeI_2 (very marked), viz., $2\text{AlMeX}_2 \rightarrow \text{AlMe}_2\text{X} + \text{AlX}_3$. The following are thus prepared: AlMeCl_2 , m.p. 72.7°, b.p. 97—101°/100 mm.; AlMe_2Cl , b.p. 83—84°/200 mm.; AlMeBr_2 , m.p. 79°; AlMe_2Br , b.p. 74—77°/50 mm., solidifies when cooled in solid CO_2 ; AlMe_2I , b.p. 109—110.5°/50 mm.; AlPr^nI_2 , m.p. 3—4°. The above reaction is unsuccessful with other Pr halides and with several Bu and amyl halides, owing to a vigorous decomp. reaction involving formation of saturated hydrocarbon of the same C content as the halide used, some Al halide, and some gummy material; this reaction also occurs sometimes (but can be controlled) with EtCl and Pr^nI . Difficultly separable mixtures of AlRX_2 and AlR_3X are treated with AlX_3 to give AlRX_2 , and with AlR_3 to yield AlR_2X . The following are thus prepared (unless stated otherwise): AlEtCl_2 , b.p. 114.5—115.5°/50 mm., m.p. 32°; AlEt_2Cl , b.p. 125—126°/50 mm.; AlEtBr_2 , b.p. 120—122.5°/10 mm., m.p. 23.5—24.4°; AlMeI_2 , m.p. 68—71° (softens at 63°); AlEtI_2 , m.p. 39—40°; AlEt_2I , from AlEt_3 and AlI_3 ; AlPhCl_2 , m.p. 94—95°, from AlPh_3 and AlCl_3 ; impure AlPhBr_2 , m.p. 73.5—87° (mostly liquid at 80°), from AlPh_3 and AlBr_3 ; AlPhI_2 , m.p. 106—110° (?); *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{AlI}_2$, m.p. 140—145° (partly from 111°). EtBr and 7:3 Al-Mg alloy (A) with a little I in N_2 at 120—140° (after initial reaction is over) give nearly pure AlEt_2Br , b.p. 75°/2 mm., and (pure) 147—148°/50 mm. (obtained during treatment of $\text{AlEtBr}_2 + \text{AlEt}_2\text{Br}$ with Na), which with Na at 105—110° and then at 200—210° affords AlEt_3 , b.p. 128—130°/50 mm.; the reaction is: $3\text{AlEt}_2\text{Br} + 3\text{Na} \rightarrow 2\text{AlEt}_3 + 3\text{NaBr} + \text{Al}$. Successive treatment of AlMeCl_2 and AlMe_2Cl with Na and Na-K alloy gives AlMe_3 , b.p. 125—126°/755 mm. AlPr^nI_2 , b.p. 153—156°/4.2—4.7 mm., is obtained from Pr^nI and (A). $\text{Al}(\text{OMe})_3$ (1 mol.) and AlMe_3 (2 mols.) at 100—135° give $\text{AlMe}_2\cdot\text{OMe}$, b.p. 87—88°/10 mm., m.p. 30—33°; with 0.5 mol. of AlMe_3 the non-volatile, infusible $\text{AlMe}(\text{OMe})_2$ results. $\text{AlEt}_2\cdot\text{OEt}$, b.p. 108—109°/10 mm., m.p. 2.5—4.5°, and $\text{AlEt}(\text{OEt})_2$, b.p. 137°/0.1 mm., are similarly prepared.

H. B.

Decomposition of organic mercury compounds HgRBr in alcohols. M. M. KOTON and F. S. FLORINSKI (J. Gen. Chem. Russ., 1939, 9, 2196—2199).—When the compounds HgRBr ($\text{R} = \text{Et}$, Pr^n , Bu^n , Ph , $\alpha\text{-C}_{10}\text{H}_7$) are heated with the alcohols $\text{CH}_2\text{R}'\cdot\text{OH}$ ($\text{R}' = \text{Me}$, Pr^n , Bu^n), the following reactions take place: $2\text{HgRBr} \rightleftharpoons 2\text{R} + 2\text{HgBr}^*$; $\text{CH}_2\text{R}'\cdot\text{OH} \rightarrow \text{R}'\cdot\text{CHO} + 2\text{H}^*$; $2\text{R} + 2\text{H}^* \rightarrow 2\text{RH}$; $2\text{HgBr}^* \rightarrow 2\text{HgBr}$; $2\text{R}'\cdot\text{CHO} \rightarrow \text{CH}_2\text{R}'\cdot\text{CO}_2\text{R}'$.

R. T.

Organo-metallic compounds. V. Formation of crystalline compounds of the type $\text{R}(\text{SnMe}_2\text{O})_3\text{OR}$, SnMe_2X_2 in alcoholic solution. VI. Thermal decomposition of tin triethyl hydroxide. VII. Effect of solvents on formation of SnMe_3Cl , $\text{SnMe}_3\cdot\text{OH}$, H_2O , and SnMe_3Cl , $[\text{SnMe}_3\cdot\text{OH}]_2$. T. HARADA (Sci. Papers Inst. Phys. Chem. Res. Japan, 1939, 36, 497—500, 501—503, 504—509; cf. A., 1939, II, 251).—V. The compounds previously described as SnR_3X , $\text{SnR}_3\cdot\text{OH}$, H_2O are now shown to be

$R(SnMe_2O)_3OR, SnMe_2X_2$ (I) ($R = \text{alkyl}$, $X = \text{Br}$ or I). The following compounds are described: $R = Et$, $X = I$, m.p. 214—218°; $R = Et$, $X = Br$, m.p. 210—215°; $R = Pr$, $X = I$, m.p. 230—235°; $R = Bu$, $X = I$, m.p. 200—209°. The mol. wt. of $Et(SnMe_2O)_3OEt, SnMe_2I_2$ in $C_{10}H_8$ approaches that of a mixture of $SnMe_2I_2, H(SnMe_2O)_3OH$ and $EtOH$ as the concn. of solute increases. (I) are easily hydrolysed by H_2O .

VI. When $SnEt_3OH$ is heated in a sealed tube at 200—220°/5 hr. C_2H_6 and $SnEt_2O$ are formed (cf. *loc. cit.*). $(SnEt_3)_2O$ is stable under these conditions, but at 270°/5 hr. gives $SnEt_2O$, $SnEt_2$, SnO , and an unidentified gas.

VII. Equimol. amounts of $SnMe_3OH$ (II) and $SnMe_3Cl$ in moist C_6H_6 give $SnMe_3Cl, SnMe_3OH, H_2O$ (III), m.p. 81—95° (decomp.) (cf. Kraus *et al.*, A., 1925, i, 1254). With 2 mols. of (II) $SnMe_3Cl, (SnMe_3OH)_2$ (IV), m.p. 85—91° (decomp.), is formed; when recrystallised from H_2O this gives (III). (III) with Ag_2O in $EtOH$ gives (I), loses H_2O when dried over $CaCl_2$ or heated with $CHCl_3$, and mol. wt. determinations in $C_{10}H_8$ indicate that the compound dissociates into H_2O , $(SnMe_3)_2O$, and $SnMe_3Cl$. When (IV) is heated with $CHCl_3$, no H_2O is formed.

J. L. D.

Lead compounds with polynuclear cations.—See A., 1940, 1, 229.

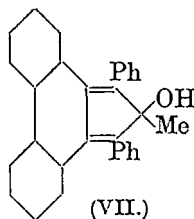
Separation of optical antipodes [*d*- and *l*- $Cr en_3Cl_3$].—See A., 1940, I, 229.

Catalytic hydrogenation of compounds having several double linkings. II. Hydrogenation of dimethylfulvene. B. A. KAZANSKI and G. T. TATEVOSJAN (J. Gen. Chem. Russ., 1939, 9, 2248—2255).—Dimethylfulvene is hydrogenated (Pd or Pt) to a product containing isopropylcyclopentane 8, isopropylidenecyclopentane 20, and isopropyl- Δ^1 -cyclopentene (I) 60%. Et cyclopentanecarboxylate and $MgMeI$ yield cyclopentylidimethylcarbinol, b.p. 77—78°/13 mm., from which (I) is obtained by dehydration with anhyd. $H_2C_2O_4$.

R. T.

Highly arylated compounds. IX. Highly arylated fulvenes. W. DILTHEY and P. HUCHTE-MANN (J. pr. Chem., 1940, [ii], 154, 238—265; cf. A., 1939, II, 84).—2:3:4:5-Tetraphenyl- $\Delta^{2:4}$ -cyclopentadienone (tetracyclone) (I) and $MgMeBr$ afford 2:3:4:5-tetraphenyl-1-methyl- $\Delta^{2:4}$ -cyclopentadienol (II), m.p. 195°, converted by boiling $HCl-AcOH$ (or $H_2SO_4-AcOH, P_2O_5-C_6H_6$, or $KHSO_4$) into 2:3:4:5-tetraphenylfulvene (III), m.p. 211—212° [$Br-CHCl_3$ give a Br_2 -adduct, m.p. 147—148°; Cl_2-Et_2O give a Cl_4 -adduct, m.p. 149° (formulae suggested); $p-NO-C_6H_4-NMe_2$ in C_5H_5N (with or without $EtOH$) and piperidine at room temp. give the corresponding anil, m.p. 217—218°], also obtained from 2:3:4:5-tetraphenyl- $\Delta^{2:4}$ -cyclopentadiene (IV) and $CH_2O-KOMe-MeOH$. (II) and cold $HCl-AcOH$ give 1-chloro-2:3:4:5-tetraphenyl-1-methyl- $\Delta^{2:4}$ -cyclopentadiene, m.p. 166—167° (indef.), decomposed by heat into (III). (III) and boiling H_2O_2-KOH -dioxan give 1:6-oxido-2:3:4:5-tetraphenylfulvene, m.p. 227°. (I) and $MgEtBr$ give 2:3:4:5-tetraphenyl-1-ethyl- $\Delta^{2:4}$ -cyclopentadienol, m.p. 188°, converted by $HCl-AcOH$ into 2:3:4:5-tetraphenyl-6-

methylfulvene, m.p. 194—195°. (I) and $CH_2Ph-MgCl$ afford 2:3:4:5-tetraphenyl-1-benzyl- $\Delta^{2:4}$ -cyclopentadienol, m.p. 156—157° (cf. Löwenbein *et al.*, A., 1926, 171), converted by HCl or $KHSO_4$ in $AcOH$ into 2:3:4:5:6-pentaphenylfulvene, m.p. 200—201° (*loc. cit.*, m.p. 204°), also prepared from (IV) and $PhCHO-KOMe-MeOH$. (IV) and $p-OMe-C_6H_4-CHO$ or $p-NMe_2-C_6H_4-CHO$ similarly give 6-*p*-anisyl-, m.p. 197—198°, and *p*-dimethylaminophenyl-2:3:4:5-tetraphenylfulvene, m.p. 207—210° (not sharp), respectively. 2:4:5-Triphenyl- $\Delta^{2:4}$ -cyclopentadiene (V) and CH_2O or $PhCHO$ in $KOMe-MeOH$ afford 2:4:5-triphenyl-, m.p. 148°, and 2:4:5:6-tetraphenylfulvene, m.p. 156°, respectively. (V) or (IV) and CCl_3Ph_2 at 190—195° give 2:4:5:6:6-penta-, m.p. 181°, and 2:3:4:5:6:6-hexa-phenylfulvene, m.p. 301—302°, respectively. 2:5-Diphenyl-3:4-(*oo'*-diphenylene)- $\Delta^{2:4}$ -cyclopentadienone (VI) and $MgMeBr$ give 2:5-diphenyl-3:4-(*oo'*-diphenylene)-1-methyl- $\Delta^{2:4}$ -cyclopentadien-1-ol (VII), m.p. 231—232°, converted by $HCl-AcOH$ into 2:5-diphenyl-3:4-(*oo'*-diphenylene)fulvene, m.p. 239—240°. (VI) and $MgEtBr$ or $CH_2Ph-MgCl$ give 2:5-diphenyl-3:4-(*oo'*-diphenylene)-1-ethyl-, m.p. 195° (previous



(VII.)

sintering), and -benzyl- $\Delta^{2:4}$ -cyclopentadienol, m.p. 271—272°, respectively. 2:5-Diphenyl-3:4-(1:8-naphthylene)- $\Delta^{2:4}$ -cyclopentadienone and $MgMeI, MgEtBr$, or $CH_2Ph-MgCl$, respectively, give 2:5-diphenyl-3:4-(1:8-naphthylene)-1-methyl- (VIII), m.p. 197° (decomp.), -1-ethyl-, m.p. 146°, and -1-benzyl- $\Delta^{2:4}$ -cyclopentadien-1-ol, m.p. 234—235°, respectively. (VIII) and $HCl-AcOH$ give 2:5-diphenyl-3:4-(1:8-naphthylene)fulvene, m.p. 225—226°. The relation between colour and constitution of the compounds is examined.

A. T. P.

Isomerisation of polymethylene hydrocarbons in presence of aluminium chloride. IV. Isomerisation of *n*-butylcyclopentane. M. B. TUROVA-POLAK and A. F. KOSCHELEV (J. Gen. Chem. Russ., 1939, 9, 2179—2183).—*n*-Butylcyclopentane, b.p. 156.2—156.8° (from cyclopentanone and $MgBu^+Br$), with $AlCl_3$ at 160—165° yields cyclohexane 80, cyclopentane 13.7, and paraffin hydrocarbons 6.3%. The cyclohexane fraction consists chiefly of hexahydro- ψ -cumene.

R. T.

Hydrogenation of cyclohexene under pressure. A. F. NIKOLAEVA and P. V. PUTSCHKOV (J. Gen. Chem. Russ., 1939, 9, 2153—2155).—cyclohexene is hydrogenated (MoS_2 catalyst, at 400°/140 atm.) to cyclohexane, with methylcyclopentane as by-product.

R. T.

Cyclic systems with a triple linking. III. Attempted introduction of a triple linking into a substituted six-membered ring. N. A. DOMNIN (J. Gen. Chem. Russ., 1939, 9, 1983—1989).—4-Methylcyclohexanone and PCl_5 (4 hr. at 50°) yield 4-chloro-1-methyl- Δ^3 -cyclohexene (I), b.p. 50—53°/16 mm., which with Br in $CHCl_3$ gives 4-chloro-3:4-dibromo-1-methylcyclohexane, b.p. 110—120°/4 mm.; this with 20% KOH in $EtOH$ yields a mixture of products, of which (I), 4-chloro-5-ethoxy-, and

3 : 4-dibromo-1-methyl- Δ^3 -cyclohexene (II), b.p. 94—95°/4 mm., were identified. (II) heated with Na in Et₂O yields resinous polymerides; the expected cyclohexinene was not obtained. R. T.

Thermal polymerisation of gaseous styrene.—See A., 1940, I, 221.

Isomerisation of allylbenzene.—See A., 1940, I, 225.

Action of aluminium chloride on aromatic hydrocarbons. II. 1 : 3-Dimethyl-4-propylbenzenes. (MISS) D. NIGHTINGALE and B. CARTON, jun. (J. Amer. Chem. Soc., 1940, 62, 280—283; cf. A., 1939, II, 102).—1 : 3 : 4-C₆H₃Me₂·COEt and Zn-Hg-HCl or *m*-xylene (I), cyclopropane, and AlCl₃ at 0—5° (later 15°) give 4-*n*-propyl-*m*-xylene (II), b.p. 95°/23 mm. [(NHAc)₂-derivative, m.p. 284°]. Pr²OH, (I), and H₂SO₄ at 0°—room temp. give 4-isopropyl-*m*-xylene (III), b.p. 77°/13 mm. [(NHAc)₂-derivative, m.p. 292°]. 5-isoPropyl-*m*-xylene (IV), b.p. 83—85°/17 mm. [(NHAc)₂-derivative, m.p. 295°], is obtained from (I) by Pr²Cl (48%) or Pr²Cl-AlCl₃ (46%) at room temp. or HCO₂Pr². 5-*n*-Propyl-xylene, b.p. 92—93° (90—91°)/18 mm. [(NHAc)₂-derivative, m.p. 239°], is obtained from COMePr², COMe₂, and H₂SO₄ at 0—10° or from mesitylene, EtI, and Na. With AlCl₃ at 85—90° (incompletely at 55°) (II) or (III) gives (IV). This renders doubtful results of Baddeley *et al.* (A., 1935, 612) and Heise *et al.* (A., 1892, 1309). R. S. C.

Identification of organic compounds. I. Chlorosulphonic acid as a reagent for the identification of aryl halides. E. H. HUNTRESS and F. H. CARTEN (J. Amer. Chem. Soc., 1940, 62, 511—514).—Addition of aryl halides or polyhalides, alone or in CHCl₃, to an excess of ClSO₃H, usually at 0°, gives in 28 cases ArSO₂Cl (usually 60—90%), converted quantitatively by conc., aq. NH₃ into ArSO₂·NH₂. In absence of CHCl₃, sulphones are thus obtained from PhF, PhI, *o*-C₆H₄Cl₂, or *o*-C₆H₄Br₂ (at 50°), and in some cases sulphones are by-products. *p*-C₆H₄I₂ gives 2 : 3 : 5 : 6-tetrachloro-1 : 4-di-iodobenzene, m.p. 210—211°, and 1 : 2 : 4 : 5-C₆H₂Cl₄ gives C₆Cl₆. The reaction failed in 10 cases. 1 : 2 : 3 : 1 : 2 : 4-, and *s*-C₆H₃Cl₃ are identified by conversion by HNO₃ (*d* 1.49) into the NO₂- or by boiling HNO₃-H₂SO₄ into the (NO₂)₂-derivatives. The following are new, orientations being assigned by analogy: (*p*-C₆H₄F)₂, m.p. 97—98°, (*p*-C₆H₄I)₂, m.p. 201—202°, (3 : 4-C₆H₃Cl₂)₂, m.p. 175—176°, and (3 : 4-C₆H₃Br₂)₂, m.p. 176—177°, sulphone; 5-chloro-1 : 3-dinitro-4 : 6-, m.p. 136—138°, and -2 : 6-dianilino-benzene, m.p. 182°, prepared from C₆HCl₃(NO₂)₂. R. S. C.

Reactivity of the methyl group. VI. Halogenonitrotoluenes. L. CHARDONNENS and P. HEINRICH (Helv. Chim. Acta, 1940, 23, 292—302).—Halogen in a suitable position can activate or increase the reactivity of Me. 1 : 2 : 4-C₆H₃MeCl·NO₂ and *p*-NO-C₆H₄·NMe₂ in boiling EtOH containing anhyd. Na₂CO₃ give 2-chloro-4-nitrobenzaldehyde-4'-dimethylaminoanil (I), m.p. 191°, and very small amounts of an unidentified brown compound (II), m.p. 303—304°. (I) is also obtained in minimal amount when condensation occurs in presence of KOH, but the main

products are *trans*-2 : 2'-dichloro-4 : 4'-dinitrostilbene and 4 : 4'-tetramethyldiaminoazoxybenzene formed from the individual reactants. Analogously, *p*-NO-C₆H₄·NEt₂ yields 2-chloro-4-nitrobenzaldehyde-4'-diethylaminoanil (III), m.p. 154—156°, with a little (II). (I) or (III) is transformed by 12% HCl in CHCl₃ into 4 : 2 : 1-NO₂·C₆H₃Cl·CHO, m.p. 74° (phenylhydrazones, m.p. 154°; 2 : 4-dinitrophenylhydrazones, decomp. 247°; semicarbazones, decomp. 234°). 1 : 2 : 4-C₆H₃MeCl·NO₂ and PhCHO in presence of a considerable proportion of piperidine at 170—180° give 2-chloro-4-nitrostilbene, m.p. 111—112° (dibromide, m.p. 172°). Analogously, *p*-NMe₂·C₆H₄·CHO yields 2-chloro-4-nitro-4'-dimethylaminostilbene, m.p. 193°. Under like conditions 1 : 2 : 4-C₆H₃MeBr·NO₂ affords 2-bromo-4-nitrostilbene, m.p. 123° (dibromide, m.p. 194°), and 4'-dimethylaminostilbene, m.p. 196°. 2-Iodo-4-nitro-stilbene, m.p. 152°, and -4'-dimethylaminostilbene, m.p. 201°, are described. *p*-NMe₂·C₆H₄·CHO gives 4-chloro-, m.p. 151°, and 6-chloro-, m.p. 108.5°, -2-nitro-4'-dimethylaminostilbene. H. W.

3 : 4-Dinitrotoluene. A. MANGINI (Atti X Congr. Internaz. Chim., 1938, III, 243—248).—A review (cf. A., 1939, II, 13, 102). E. W. W.

Preparation of substituted diphenyldiacetylenes. J. S. SALKIND and B. M. FUNDLER (J. Gen. Chem. Russ., 1939, 9, 1725—1728).—When substituted acetylenes are heated at 55—60° with CuCl and NH₄Cl in dil. HCl, the reaction is 2C₆H₄R·C≡CH → (C₆H₄R·C≡C)₂ (R = *p*-Me, H, *p*-Cl, *p*-Br, and *p*-NO₂). The following are thus obtained: di-(*p*-chloro-), m.p. 258°, -bromo-, m.p. 263—264°, and -nitro-phenyl)diacetylene, m.p. 285—286°. R. T.

Seleniated benzyl derivatives. G. SPERONI and B. SMI (Atti X Congr. Internaz. Chim., 1938, III, 358—363).—Se in conc. Na₂S shaken with *o*-NO₂·C₆H₄·CH₂Cl in Et₂O gives a substance, C₇₀H₆₀N₂₀S₄Se₆ (I), orange-yellow, m.p. 103.5°; a yellow form is also obtained, from solvents, and is converted into the orange-yellow below the m.p. (I) is also obtained from (*o*-NO₂·C₆H₄·CH₂·Se)₂ (A) and (*o*-NO₂·C₆H₄·CH₂·S)₂ (B) in C₆H₆, and is apparently 3A,2B. Thermal analysis of mixtures of A and B indicates compound-formation. Using 5 : 2 : 1-NO₂·C₆H₃Cl·CH₂Cl and Se in Na₂S, a compound, C₇₀H₅₀O₂₀N₁₀S₄Se₆Cl₁₀, m.p. 165.5°, is obtained. E. W. W.

Rates of reaction of *p*-alkylbenzhydryl chlorides with ethyl alcohol.—See A., 1940, I, 222.

Hydroaromatic hydrocarbons of the naphthalene and tetrahydronaphthalene series, with cyclopentane as substituent. E. S. POKROVSKAJA and R. J. SUSCHTSCHIK (J. Gen. Chem. Russ., 1939, 9, 2291—2301).—C₁₀H₈ heated with cyclopentene and AlCl₃ yields mixtures of isomeric mono-, di-, tri-, tetra-, m.p. 135—136°, and penta-cyclopentyl-naphthalene, m.p. 176—177°. Mixtures of isomeric mono-, di-, tri-, and tetra-cyclopentyltetrahydronaphthalenes are obtained analogously. Mono- and di-cyclopentyldecahydronaphthalene (isomerides) were obtained by hydrogenation (Pt-C) of the corresponding tetrahydronaphthalenes. R. T.

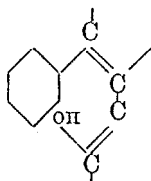
Naphthalene derivatives. I. Action of chlorates on naphthalenemonosulphonic acids. V. V. KOZLOV and D. G. TALIBOV (J. Gen. Chem. Russ., 1939, 9, 1827—1833).— $1\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$ and KClO_3 in aq. HCl at 20° yield 5:1- and 8:1- $\text{C}_{10}\text{H}_6\text{ClSO}_3\text{H}$. At $50\text{--}60^\circ$, 1:5-, 1:6-, and 1:8- $\text{C}_{10}\text{H}_6\text{Cl}_2$ are obtained, whilst at 100° the products are 1:5-, 1:6-, 1:7-, and 1:8- $\text{C}_{10}\text{H}_6\text{Cl}_2$. 1:6- and 1:7- $\text{C}_{10}\text{H}_6\text{Cl}_2$ undergo oxidation in these conditions, to yield 6-chloro-1:4-naphthaquinone, m.p. $106\text{--}107^\circ$. The products obtained similarly with $2\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$ are 5:2- and 8:2- $\text{C}_{10}\text{H}_6\text{ClSO}_3\text{H}$ at $20\text{--}50^\circ$, and 2:6-, 1:6-, and 1:7- $\text{C}_{10}\text{H}_6\text{Cl}_2$ at 100° . R. T.

Polycyclic homologues of naphthalene and tetrahydronaphthalene. E. S. POKROVSKAJA and T. G. STEPANTZEVA (J. Gen. Chem. Russ., 1939, 9, 1953—1960).—cycloHexene in CS_2 and C_{10}H_8 condense in presence of AlCl_3 to a mixture of mono-, di-, tri-, m.p. $121\text{--}122^\circ$, and 2:3:6:7-tetra-cyclohexylnaphthalene, m.p. 269° . Two isomeric dicyclohexylnaphthalenes were isolated, one of m.p. $150\text{--}151^\circ$, and the other an oil, b.p. $203\text{--}206^\circ/3\text{ mm.}$, f.p. 3° . The former was dehydrogenated (Pt-C at 310°) to a diphenylnaphthalene, m.p. 230° . Tetrahydronaphthalene, condensed similarly, yields mono- (I), b.p. $147\text{--}149^\circ/3\text{ mm.}$, f.p. -2° , and di-cyclohexyltetrahydronaphthalene, b.p. $198\text{--}203^\circ/3\text{ mm.}$, f.p. -4° . (I) was hydrogenated (Pt, at $170\text{--}180^\circ$) to a mixture of α - and β -cyclohexyldecahydronaphthalene. Solubilities of the above products in kevulic and pyruvic acid are given. R. T.

Passage from the diphenyl to the fluorene system: preparation of 2:6-, 2:7-, and 3:5-dimethylfluorene. B. LONGO (Atti X Congr. Internaz. Chim., 1938, III, 239—240).—By Mascarelli's method, in which $2':2\text{-NO}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{Me}$ is converted, through the $2'\text{-NH}_2$ - and $2'\text{-OH}\cdot\text{N}_2$ -compounds, into fluorene, 2'-nitro-2:5:4'-, -2:4:4'-, and -2:5:6'-trimethylidiphenyl are converted respectively into 2:6-, m.p. $66\text{--}67^\circ$, 2:7-, m.p. $114\text{--}115^\circ$, and 3:5-dimethylfluorene, m.p. $81\text{--}82^\circ$.

E. W. W.

New route to 9-alkyl- and 9-aryl-anthracenes. C. K. BRADSHAW (J. Amer. Chem. Soc., 1940, 62, 486—488).—A general synthesis is described. $o\text{-C}_6\text{H}_4\text{Cl-CH}_2\text{Ph}$ (prep. in 81% yield from $o\text{-C}_6\text{H}_4\text{Cl-CHPh-OH}$ by red P-I-AcOH- H_2O), b.p. $144^\circ/5\text{ mm.}$, and CuCN at 250° give 54% of $o\text{-CN-C}_6\text{H}_4\text{-CH}_2\text{Ph}$, b.p. $160\text{--}164^\circ/4\text{ mm.}$, and thence by MgMeI in Et_2O , later boiling C_6H_6 , 72% of *o*-benzylacetophenone, m.p. $49\text{--}50^\circ$. Boiling 34% aq. HBr-AcOH (1:1) then gives (4 days) 80% of 9-methylanthracene, m.p. $80\text{--}81^\circ$. Similarly are prepared *o*-benzyl-propio-phenone, b.p. $156^\circ/3\text{ mm.}$ (unstable phenylhydrazone, m.p. $97\text{--}98^\circ$), and -benzophenone, m.p. $50\text{--}52^\circ$, b.p. $199\text{--}200^\circ/3\text{ mm.}$, 9-ethyl- (69%), m.p. $58\text{--}59^\circ$, and 9-phenyl-anthracene (75%), m.p. $154\text{--}155^\circ$. Cyclisation probably



occurs by way of the enolic form (annexed), the conjugation labilising the nuclear H and the slow rate of enolisation accounting for the necessary long period of reaction.

R. S. C.

K (A., II.)

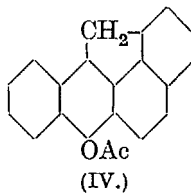
Diterpenes. XXXIX. 6-Ethylretene. L. RUZICKA and S. KAUFMANN (Helv. Chim. Acta, 1940, 23, 288—291).—Me 6-acetyldehydroabietate (I), m.p. $132\text{--}133^\circ$, is reduced (Clemmensen) to Me 6-ethyldehydroabietate, m.p. $94.5\text{--}95^\circ$, $[\alpha]_D +60\pm0.6^\circ$ in CHCl_3 , which is converted by Se at $320\text{--}330^\circ$ into 6-ethylretene (II), m.p. $80\text{--}80.5^\circ$ [picrate, m.p. $148\text{--}149^\circ$; additive product, m.p. $169.5\text{--}170.5^\circ$, with $\text{C}_6\text{H}_3(\text{NO}_2)_3$]. This is oxidised by CrO_3 in AcOH to 6-ethylretenequinone, m.p. $198\text{--}198.5^\circ$ (quinoxaline derivative, $\text{C}_{26}\text{H}_{24}\text{N}_2$, m.p. $174\text{--}175.5^\circ$). (II) is also obtained by the action of Se on (I). H. W.

Benzopyrenes from 6-alkyl- or 6-aryl-benz-anthrones. (SIGNA.) E. GHIGI (Atti X Congr. Internaz. Chim., 1938, III, 178—182).—6-*n*-Propylbenzanthrone (I) is unchanged by NaOH-MeOH , or by P_2O_5 at 165° . With AlCl_3 at 165° it gives benzanthrone; with POCl_3 an amorphous product (II), m.p. $250\text{--}260^\circ$, is formed. With Zn-AcOH , (I) gives a product, m.p. $\sim 130^\circ$, which with POCl_3 also gives (II). Distillation of (I) from Zn gives 1:2-benzopyrene (cf. Cook, A., 1933, 601), oxidised by $\text{CrO}_3\text{-AcOH}$ to a substance, m.p. 225° . E. W. W.

Photo-oxides of carcinogenic hydrocarbons. C. B. ALLSOPP (Nature, 1940, 145, 303; cf. A., 1939, II, 413).—Irradiation of 3:4-benzopyrene (I) in C_6H_6 with the 2536 Å. Hg resonance line, followed by evaporation of the C_6H_6 , yields a coloured residue which, on extraction with H_2O or dil. NaHCO_3 , gives a colourless solution possessing a characteristic absorption spectrum. The spectrum indicates that a labile photo-oxidation product can be prepared from (I). Addition of the extract to chick heart tissue cultures produces a high % of abnormal mitotic cells. Irradiation of C_6H_6 under similar conditions yields a small oily residue which dissolves in H_2O to a yellow solution having a well-defined absorption band at 2760 Å.

L. S. T.

***o*-Halide synthesis of 10-methyl-9:1'-methylene-1:2-benzanthracene.** L. F. FIESER and J. CASON [with, in part, E. M. GROSS] (J. Amer. Chem. Soc., 1940, 62, 432—436).—Acenaphthene and 85—90% Pb_3O_4 in AcOH [reacts as $\text{Pb}(\text{OAc})_4$] at $60\text{--}70^\circ$ gives 7-acenaphthenyl acetate, hydrolysed by boiling $\text{KOH-MeOH-H}_2\text{O}$ to 7-acenaphthenol (70.5—74% overall yield), m.p. $144.5\text{--}145.5^\circ$ (lit. 146° , 148°). $\text{CrO}_3\text{-AcOH}$ at $28\text{--}32^\circ$ then gives 7-acenaphthenone (I) (65%), m.p. $121\text{--}121.5^\circ$, converted by $o\text{-C}_6\text{H}_4\text{Cl-MgBr}$ in $\text{Et}_2\text{O-C}_6\text{H}_6$ into 7-*o*-chlorophenyl-7-acenaphthenol (15—20%), m.p. (crude) $216\text{--}218^\circ$ (decomp.); dehydration of the crude product by boiling AcOH and purification by adsorption on activated Al_2O_3 and "supercel" gives 33—36% [calc. from (I)] of 7-*o*-chlorophenylacenaphthylene (II), m.p. $104\text{--}104.4^\circ$. With $\text{H}_2\text{-PtO}_2$ in $\text{AcOH-Et}_2\text{O}$, this gives 7-*o*-chlorophenylacenaphthene, m.p. $81\text{--}82^\circ$, b.p. $190\text{--}192^\circ/2\text{ mm.}$, which with CuCN and a little MeCN in $\text{C}_5\text{H}_5\text{N}$ at $243\text{--}245^\circ/800\text{ lb. (N}_2\text{)}$ yields 7-*o*-cyanophenylacenaphthene (87%), m.p. $79.7\text{--}80.5^\circ$, hydrolysed by KOH in boiling, aq. EtOH (250 hr.) (higher temp. causes decomp.) to 7-*o*-acenaphthylbenzoic acid (III), m.p. 195--



195.5°; hydrolysis for 100 hr. gives the *amide*, m.p. 182—182.8°. Ac_2O - AcOH and a little ZnCl_2 cyclise (II) to 10-*acetoxyl*-9:1'-*methylene*-1:2-*benzanthr*acene (IV) (83%), softens at 171°, m.p. 175—179°, converted by Zn -alkali into 9:1'-*methylene*-1:2-*benzanthr*acene (V) (51.5%). With HF at room temp., (III) gives an anthrone (difficult to purify), which with MgMeCl in Et_2O gives 43—54% of 9:1'-*methylene*-1:2-*benz*-10-*anthranol*, m.p. 160—164° (decomp.) [with Zn -alkali gives 35% of (V), but is decomposed during other reactions], with only 1.1—1.9% of 10-*methyl*-9:1'-*methylene*-1:2-*benzanthr*acene, m.p. 181—181.4° [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 182.5—183.2°]. M.p. are corr. R. S. C.

Steroids and sex hormones. LXI. Synthesis of 1-methylchrysene. L. RUZICKA and R. MARKUS (Helv. Chim. Acta, 1940, 23, 385—388).—Gradual addition of $\text{Ph}[\text{CH}_2]_3\text{MgBr}$ to 5-keto-1-methyl-5:6:7:8-tetrahydronaphthalene in Et_2O and dehydration of the product in presence of I at 150° yields 5- β -phenylethyl-1-methyl-7:8-dihydronaphthalene, b.p. 149—150°/0.1 mm., dehydrogenated ($\text{Pd}-\text{C}$ at 280—320°) to 5- β -phenylethyl-1-methylnaphthalene, b.p. 145°/0.1 mm. This is cyclised by AlCl_3 in CS_2 to 1-methylchrysene, m.p. 254—255° [additive compound, m.p. 174—176°, with $\text{C}_6\text{H}_3(\text{NO}_2)_3$], in very poor yield. All m.p. are corr. H. W.

Detection and determination of benzedrine.—See B., 1940, 323.

Behaviour of the amino-group in solid-liquid systems with organic components.—See A., 1940, I, 215.

Exchange reaction of nuclear hydrogen of aniline hydrochloride.—See A., 1940, I, 222.

Formation of chloroaniline during reduction of nitrobenzene. G. R. ROBERTSON and R. A. EVANS (J. Org. Chem., 1940, 5, 142—145).—The approx. yields of $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ (I) obtained during reduction of PhNO_2 with the following metals (slight excess; moss or turnings except where stated) in conc. HCl are: Fe 0; Sn 3; Sn (rotated rod) 7.5; Zn 26—27; Zn (rotated rod) 9.5—11.5 (3 at 25°); $\text{Zn}-\text{Sn}$ (9:1) 23; $\text{Zn}-\text{Sn}$ (1:9) 6.7; $\text{Zn}-\text{Cu}$ (1.2%) 4; Cd 23—24; Al , Ca , Mg , no reduction; Mg (cooled in solid CO_2) 62—66%. The amount of (I) apparently varies directly with the rate of the wasteful reaction of the metal with the acid to give H_2 , indicating that either a zone of neutral solution is maintained at the surface of a more active metal (thus hindering complete reduction of the NO_2 -group) or that the excessive output of H_2 drives away the PhNO_2 before it is completely reduced. Incompletely reduced mols. are then rearranged to (I). H. B.

p-Cymene. IV. Mononitration of 2-amino-p-cymene. Preparation of 3-amino-p-cymene and o- and p-cymylenediamine. T. F. DOUMANI and K. A. KOBE (J. Amer. Chem. Soc., 1940, 62, 562—565).—2-Formamido-p-cymene, m.p. 108.8—109.4°, and $\text{H}_2\text{SO}_4\text{-HNO}_3$ at 0° give a mixture, separated by hydrolysis (30% NaOH) and distillation at 1 mm. into 3- (I) (70%), b.p. 142.9°/5 mm. [Ac , m.p. 167.6—167.8°, HCO , softens at 128°, m.p. 139.6—140°, and Bz derivative, m.p. 193.4—193.8°; previ-

ously (Wheeler *et al.*, A., 1928, 54) considered to be (II)], and 5-nitro-2-amino-p-cymene (II) (30%), m.p. 66.6—67.6° (Ac , m.p. 142.8—143.2°, HCO , m.p. 101.6—102.2°, and Bz derivative, m.p. 139.0—139.4°). Nitration of 1:4:2- $\text{C}_6\text{H}_3\text{MePr}^{\beta}\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_4$ gives ~60% of (I) and 40% of (II), and that of its Ac derivative (later hydrolysis) gives 52% of (I) and 48% of (II). Structures are proved as follows. Zn dust- EtOH -30% NaOH reduces (I) to o-cymylenediamine, m.p. 95.0—95.8° (Ac_2 derivative, m.p. 235.1—235.3°), which yields 2:7-dimethyl-4-isopropylbenzimidazole, m.p. 179.5—179.9°, 2:3-diphenyl-5-methyl-8-isopropylquinoxaline, m.p. 136.7—137.3°, and 6-methyl-9-isopropyl-1:2:3:4-dibenzphenazine, m.p. 181.2—181.4°. Reduction of (II) gives p-cymylenediamine, m.p. 50.0—50.5° (Ac_2 derivative, m.p. 262.0—262.2°), oxidised by FeCl_3 to thymoquinone. 3-Nitro-p-cymene, b.p. 116.7°/10 mm., is obtained in ~52% yield from (I), (II), or the crude mixture thereof, and is reduced by $\text{Fe}-\text{HCl}$ to 3-amino-p-cymene, b.p. 105.7°/10 mm., 240.2°/760 mm. (HCO derivative, m.p. 106.2—106.6°), which by diazotisation yields thymol. M.p. are corr. R. S. C.

Complex salts of cobalt^{III} with dimethylglyoxime [and aromatic amines]. A. ABLOV (Bull. Soc. chim., 1940, [v], 7, 151—164).—Passage of air through a solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (1 mol.), dimethylglyoxime (I) (2 mols.), and NH_2Ph (2 mols.) in EtOH at room temp. gives the non-electrolyte $[\text{Co}(\text{DH})_2\text{RCl}]\cdot 2\text{H}_2\text{O}$ [$\text{DH}_2 = (\text{CMe}\cdot\text{N}\cdot\text{OH})_2$ and $\text{DH} = \text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{NO}\cdot$; $\text{R} = \text{NH}_2\text{Ph}$]; the corresponding bromide (+2 H_2O), iodide (+0.5 H_2O), and thiocyanate are obtained if CoCl_2 is replaced by $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O} + \text{NaBr}$, + KI , and + NH_4CNS , respectively. By suitably altering the base similar Cl-derivatives are analogously obtained in which $\text{R} = o$ - or p - (+ H_2O)- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, o -, m - and p - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, m - and p - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (both +2 H_2O), and p - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$; analogous Br - and I -compounds where R is m - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and p - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (+3 and 1 H_2O , respectively) are described. In the case of sufficiently strong bases salts $\text{X}[\text{Co}(\text{DH})_2\text{R}_2]$ result if <3 mols. of base are used. Chlorides are described in which $\text{R} = \text{NH}_2\text{Ph}$ (+4 H_2O), m - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ [also corresponding bromide, iodide, and nitrate (+2 H_2O)], p - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ [also corresponding bromide and nitrate (+ H_2O)], p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ [also corresponding nitrate (+ H_2O)], m - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ [also bromide and nitrate (+ H_2O)], o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, m - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (also bromide), p - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (bromide only), and o - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (also iodide). The less powerful bases give these salts only if used in large excess and pure compounds cannot always be obtained. p - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ gives only the non-electrolyte type whereas the very weak o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ cannot be introduced into the complex. If air is passed into the mixture of this base, (I), and CoCl_2 the product is Feigl's green chloride, also obtained in the absence of base. The complex, $[\text{Co}(\text{DH})_2(\text{DH})\text{I}_2]$, is described. H. W.

Nitrosoacylarylamines. II. Action of nitrous fumes on acylarylamines. J. W. HAWORTH and D. H. HEY [with E. C. BUTTERWORTH] (J.C.S., 1940, 361—369; cf. A., 1938, II, 92).—The action of

nitrous fumes on acylarylamines in AcOH (or AcOH-Ac₂O) at 10° shows that they may be divided into four classes, viz., those which (A) give *N*-NO-derivatives which react with C₆H₆, e.g., NO·NR·COR' + C₆H₆ → RPh + N₂ + R'CO₂H; (B) give NO-derivatives not reacting with C₆H₆, (C) react but do not give NO-derivatives, and (D) do not react. Examples of class (A) (m.p. of NO-derivative in brackets) are: HCO·NHPh [m.p. 45–46° (decomp.)], EtCO·NHPh [m.p. 52° (decomp.)], ω-chloro- [m.p. 65° (decomp.)], and -bromo-acetanilide [m.p. 54–55° (decomp.)], acet-*p*-aniside [m.p. 83–84° (decomp.)], -*p*-phenetide [m.p. 60° (decomp.)], -α- [m.p. 57° (decomp.)] and -β-naphthalide [m.p. 80° (decomp.)] (cf. A., 1935, 828). *p*-C₆H₄(NHAc)₂ and (C₆H₄·NHAc-*p*)₂ give (NO)₂-compounds which with C₆H₆ give *p*-terphenyl and *p*-ter- + *p*-quater-phenyl, respectively. Dinitroso-succindianilide detonates at 111°. Me₂ succinate and *m*-C₆H₄Cl·NH₂ give 3 : 3'-dichlorosuccindianilide, m.p. 225–226° [stable (NO)₂-compound, m.p. 105–106° (decomp.)], and *N*-*m*-chlorophenylsuccinimide, m.p. 119–120°. CO(NHPh)₂ (I) gives a NO-compound, m.p. 105° (cf. Ryan *et al.*, A., 1923, i, 380) [also prepared from NH·C(NHPh)₂, probably through (I)], converted by C₆H₆ into Ph₂ and PhNCO. 4 : 4'-Dimethyl-, 3 : 3'- and 4 : 4'-dichloro-diphenylcarbamide give NO-compounds, m.p. 92° (decomp.), 106° (decomp.), and 118° (decomp.), respectively. In class (B) are *o*-C₆H₄Cl·NHAc [NO-derivative, m.p. 59° (decomp.)], 4 : 2 : 6 : 1-NO₂-C₆H₂Cl₂·NHAc [m.p. 100° (decomp.)], and phenylurethane [m.p. 60–61° (decomp.)]; with C₆H₆, the NO-derivatives regenerate the acylarylamine. Nitroso-1-acetamido-2-methylanthraquinone, m.p. 106° (decomp.), is converted by C₆H₆ into 6 : 7-phthalylindazole. Class (C) : 4-dimethylamino-4'-acetamidazobenzene gives *p*-NO₂-C₆H₄·NMe₂, whilst NHPhBz or *p*-C₆H₄Me·NHBz affords ArN₂·NO₂, and *m*-C₆H₄(NHAc)₂ gives *m*-NHAc·C₆H₄·N₂·NO₂, converted by H₂O into *m*-NHAc·C₆H₄·OH. Class (D) : *p*-NO₂-C₆H₄·NHAc, *m*- and *p*-NO₂-C₆H₄·NHBz, PhSO₂·NHPh, *p*-C₆H₄Me·SO₂·NHPh, (CO·NHPh)₂, NHPh·CO·CO₂H, 3 : 3'-dichloro-oxanilide, 3-chloro-oxanilic acid, 3 : 3'- and 4 : 4'-dinitrodiphenylcarbamide, and 1- and 2-acetamidoanthraquinone. *p*-Benzamidoacetanilide, m.p. 230°, and nitrous fumes in Ac₂O-AcOH give *p*-benzamidonitrosoacetanilide, m.p. 116° (decomp.), converted by C₆H₆ at 70° into 4-benzamidodiphenyl. Results of the above and allied reactions are discussed.

A. T. P.

Nitrosoacylarylamines. III. New method of preparation. H. FRANCE, I. M. HEILBRON, and D. H. HEY (J.C.S., 1940, 369–371; cf. preceding abstract).—NHArAc and NOCl in AcOH (or AcOH-Ac₂O)-KOAc + P₂O₅ usually give NArAc·NO in better yield and shorter time than does the nitrous fumes method. Thus NPhAc·NO, *o*-, *m*-, and *p*-NO₂-C₆H₄·NArAc·NO, m.p. 72° (decomp. 75°) (not obtained with nitrous fumes) [converted by C₆H₆ into ~60% of *o*-, *m*-, and *p*-C₆H₄Ph·NO₂, respectively], are prepared. 2 : 4 : 1-(NO₂)₂C₆H₃·NHAc gives an oily NO-compound converted into 2 : 4-dinitrodiphenyl (10% yield). NHPhBz and *p*-NO₂-C₆H₄·NHBz give NO-compounds, decomp. 83° and 90°, respectively.

m- and *p*-C₆H₄(NHAc)₂ give (NO)₂-compounds, an oil and decomp. 124°, respectively, and thence *m*- or *p*-terphenyl, respectively. 3-Acetamidodiphenyl gives a NO-derivative, m.p. 78° (decomp.) (cf. A., 1939, II, 473), which with C₆H₆ at 20° affords *m*-terphenyl. 4 : 1 : 2-NHAc·C₆H₃(CO₂Et)₂ gives a NO-compound (an oil), and thence 4 : 1 : 2-C₆H₃Ph(CO₂Et)₂ (cf. A., 1938, II, 492). *o*-NHAc·C₆H₄·CO₂Et and 2 : 1 : 4-OMe·C₆H₃(NHAc)₂ give NO-compounds (oils). (CO·NHPh)₂, 2 : 4 : 6 : 1-(NO₂)₃C₆H₂·NHAc, and 2 : 5 : 1 : 4-(OEt)₂C₆H₂(NHAc)₂ are unchanged. NHPhAc, NOCl, and KOAc + P₂O₅ in C₆H₆ at 5–30° give Ph₂ (40% yield) directly.

A. T. P.

Condensation of butaldehyde and aniline. M. S. KHARASCH, I. RICHLIN, and F. R. MAYO (J. Amer. Chem. Soc., 1940, 62, 494–497).—NH₂Ph and PrⁿCHO give up to 78% of the dimeride (I), m.p. 92.5°, of CHPrⁿ·NPh, but in presence of a trace of org. acid give γ-anilomethyl-Δⁿ-*n*-heptene (II), b.p. 146–148°/15 mm. (II) is obtained when (I) is treated with an org. acid or kept in air (not in vac.). The structure of (II) is shown by prep. from NH₂Ph and CHPrⁿ·Cet·CHO (III), by conversion into NHPhBz and NHPhAc by BzCl and AcCl, respectively, and into the 2 : 4-dinitrodiphenylhydrazone and semicarbazone of (III) by the appropriate reagents, and by cryoscopy (CHPh₃; C₆H₆). This confirms the structure, NPh·CH·CHEt·CHPrⁿ·NPh, for (I), which is substantiated by hydrogenation (Raney Ni; 1 H₂; 100 atm.) to δ-anilino-γ-anilomethyl-*n*-heptane, b.p. 240–245°/20 mm. (Ac₂ derivative, m.p. 131°; dihydrochloride). In CHPh₃ (Rast), (I) is dimeric, but it is 40–50% dissociated in camphor. 3-Ethyl-2-*n*-propylquinoline (IV), b.p. 182–184°/23 mm. [methiodide, m.p. 160–165° (lit. 172°); hydriodide, m.p. 171–172°], is obtained by the action of 12N-HCl on (a) PrⁿCHO and NH₂Ph [NHPhBuⁿ and ? H₂- and H₄-derivatives of (IV) also formed], (b) (I), (c) NH₂Ph and (III), or (d) (II) [by dissociation into (III) and NH₂Ph and addition thereof to give NHPh·CHPrⁿ·CHEt·CHO]. *N*-Phenyl-*N'*-α-naphthyl-*N*-*n*-butylcarbamide has m.p. 277°.

R. S. C.

Action of aromatic amines on 2-iodo-5-nitro-styrene. D. E. WORRALL and F. BENINGTON (J. Amer. Chem. Soc., 1940, 62, 493–494).—*o*-C₆H₄I·CHO, MeNO₂, and NEt₃ give 65–70% of *o*-iodo-β-nitrostyrene, m.p. 113–114° (with KMnO₄ gives 5 : 2 : 1-NO₂·C₆H₃I·CO₂H), converted by fuming HNO₃ into 2-iodo-5 : β-dinitrostyrene (I), m.p. 145–146°, and by bromination followed by nitration into x-bromo-2-iodo-γ : β-dinitrostyrene, m.p. 136–137°. Org. bases add very readily to (I), yielding α-nitro-β-anilino-, m.p. 115–116° (decomp. here and below), -*o*-, m.p. 168–170°, -*m*-, m.p. 113–114°, and -*p*-toluidino-, m.p. 130–132°, -*o*-, m.p. 146–148°, -*m*-, m.p. 140–142°, and -*p*-anisidino-, m.p. 123–124°, -phenylhydrazino-, m.p. 142–144°, -β-naphthylhydrazino-, m.p. 143–144°, -hydroxylamino-, m.p. 103–105°, and -semicarbazido-, m.p. 187–188°, -β-2-iodo-5-nitrophenylethane. NH₃-C₆H₅ and (I) give di-(β-nitro-α-2-iodo-5-nitrophenylethyl)amine, m.p. 113–114° (decomp.).

R. S. C.

Relative reactivities of organometallic compounds. XXVIII. Halogen-metal interconver-

sion with *m*- and *p*-bromodimethylanilines. H. GILMAN and I. BANNER (J. Amer. Chem. Soc., 1940, 62, 344—345).—*m*- (prep. by Me_2SO_4 -aq. KOH in 54% yield) and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2$ with LiBu^+ in $\text{Et}_2\text{O} + \text{N}_2$ undergo only exchange of Br for Li, yielding after carbonation $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (*m*- 26%; *p*- 41%). Prep. of *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2$ in 70% yield by Me_2SO_4 -KOH is described. R. S. C.

Nuclear alkylation of aromatic bases. IV. Action of *n*-dodecyl alcohol on α - and β -naphthylamine hydrochlorides. E. C. BUTTERWORTH and D. H. HEY (J.C.S., 1940, 388—390; cf. A., 1937, II, 57).—*n*- $\text{C}_{12}\text{H}_{25}\cdot\text{OH}$ (I) (3 mols.) and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$ (1 mol.) at 220° (open vessel) or 240—260° (autoclave) give $\text{NH}(\text{C}_{12}\text{H}_{25})_2$ (II), $(\text{C}_{12}\text{H}_{25})_2\text{O}$ (III), Δ^2 -dodecene (IV), β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, $\text{NH}(\text{C}_{10}\text{H}_7)_2$, and *N*-dodecyl- β -naphthylamine (V), m.p. 41.5—43.5° (more formed in open vessel). Similarly, (I) and α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$ at 240—260° (autoclave) give α - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, (II), (III), (IV), and a tar. (III) and (IV) are formed from (I) + dry HCl at 250°, but action of heat on (V) may give some (IV). No nuclear alkylation is detected; the ease with which higher aliphatic alcohols lose H_2O renders them unsuitable for use in the Hofmann-Martius reaction. A. T. P.

Action of formaldehyde on sulphanilic acid. H. E. FIERZ-DAVID and L. BLAGNEY (Helv. Chim. Acta, 1940, 23, 213—218).— CH_2O and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (I) at 50° give *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (II) [isolated as the Na salt (+4 H_2O) (III) in ~10—15% yield] and an unidentified compound which gives a sparingly sol. Pb salt and regenerates (I) when treated with dil. HCl. The yield of (III) is not improved by increase in the amount of CH_2O or by addition of HCO_2H . At 100° (II) gradually disappears with formation of an approx. equiv. amount of H_2SO_4 . (III) is also obtained from (I), Me_2SO_4 , and NaOH. (III) is transformed by NaNO_2 and HCl into 2-nitro-4-dimethylaminobenzenesulphonic acid, identical with that obtained from 2:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_3\text{Na}$ and NHMe_2 . Addition of CH_2O to a solution of (I) and NPhMe_2 in H_2O leads to *N*-*p*-dimethylaminobenzylsulphanilic acid, converted by NPhMe_2 at 100° into $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$. H. W.

Sulphanilamide derivatives. VI. Substituted *N*¹-aliphatic sulphanilamides. M. L. CROSSLLEY, E. H. NORTHEY, and M. E. HULTQUIST (J. Amer. Chem. Soc., 1940, 62, 532—534).—By standard methods are obtained: *sulphanil-n-octyl*-, m.p. 114—119.5°, *-n-dodecyl*-, m.p. 118—124°, *-n-octadecyl*-, m.p. 127—130°, Δ^1 -*-n-octadecenyl*-, m.p. 118—122.5°, *-difurfuryl*-, m.p. 134—136.5°, *-methyl- β -hydroxyethyl*-, m.p. 124.5—126.3°, and *- β -sulphanilamidoethyl- β' -hydroxyethyl*-, m.p. 163—164.5°, *-amide*; $\alpha\beta$ -*di(sulphanilamido)*-, m.p. 229.4—231.2°, and $\alpha\beta$ -*di(sulphanilysulphanilamido)-ethane*, m.p. >118° (decomp.); *N*¹-*di(sulphanilamidoethyl)sulphanilamide trihydrochloride*, m.p. 241.5—244°; *sulphanil- β -hydroxy*-, m.p. 154—155.8°, and $\beta\beta'$ -*dihydroxy-tert.-butylamide*, m.p. 131.8—134°; $\alpha\gamma$ -*disulphanilamidopropan- β -ol*, m.p. 184.2—186.5°; *N*- β -*sulphonamidoethylmorpholine*, m.p. 98—100.4°; *Et sulphanilamidoacetate*, m.p. 90.4—92°; *Bu*₂-*N-sulphanilylglutamate hydrochloride*,

m.p. 138.4—141.6°. *p*-Nitrobenzenesulphon- β -hydroxyethylamide, m.p. 126—127°, and $\text{C}_{11}\text{H}_{23}\cdot\text{COCl}\cdot\text{C}_5\text{H}_5\text{N}$ at 90—100° give the dodecyl ester, m.p. 72—73.5°, reduced by $\text{Fe}\cdot\text{HCl}$ in $\text{PhMe}\cdot\text{H}_2\text{O}$ to β -*sulphanilamidoethyl dodecoate*, m.p. 63.4—64.8°. The amides are not or only slightly antistreptococcal.

R. S. C.

Conversion of sulphanilamide into *p*-hydroxylaminobenzenesulphonamide by ultra-violet irradiation. L. E. SHINN, E. R. MAIN, and R. R. MELLON (Proc. Soc. Exp. Biol. Med., 1939, 42, 736—738).—On adding Ac_2O to a mixture of these two substances the free amine is acetylated and prevented from undergoing diazotisation, so that the $\text{OH}\cdot\text{NH}$ -derivative alone gives the usual colour reaction (cf. Rosenthal and Bauer, A., 1940, III, 242). 6% of sulphanilamide is converted by 2 min. irradiation.

V. J. W.

p-Aminobenzenesulphonamide derivatives. N. S. DROZDOV and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1939, 9, 1642—1646).—The appropriate base with *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ (I) yields *p*-acetamidobenzenesulphon- (8-diethylamino- α -methylbutyl)-, -(γ -piperidino- β -hydroxypropyl)-, and -(γ -diethylamino- β -hydroxypropyl)-amide, all oils, hydrolysed (conc. HCl) to the corresponding *p*- NH_2 -compounds, m.p. 198—200° (II), 151—152°, and an oil. (I) and (II) are condensed further to *p*-(*p*-acetamidobenzenesulphonamido)benzenesulphon- (8-diethylamino- α -methylbutyl)amide, an oil. *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and (II) with $\text{NEt}_2\cdot[\text{CH}_2]_3\cdot\text{Cl}$ (14 hr. at 130—140°) give *p*- γ -diethylaminopropylaminobenzenesulphonamide, an oil, and 8-diethylamino- α -methylbutylamide, respectively. (II) in aq. HCl diazotised and coupled with β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ or *H*-acid yields respectively *p*-(2'-hydroxy-1'-naphthalene)-, m.p. 158°, and (as Na_2 salt) *p*-(8'-amino-1'-hydroxy-3':6'-disulpho-2'-naphthalene)-azobenzenesulphon- (8-diethylamino- α -methylbutyl)amide. R. T.

Fluorine and chlorine derivatives of sulphanilamidobenzenesulphonic acids. C. M. SUTER and A. W. WESTON (J. Amer. Chem. Soc., 1940, 62, 604—606).—*p*- $\text{C}_6\text{H}_4\cdot\text{F}\cdot\text{NHAc}$ (I) and 100% H_2SO_4 at 170—180° [*p*- $\text{C}_6\text{H}_4\cdot\text{F}\cdot\text{NH}_2$ (II) is unchanged] give 4-fluoroaniline-2-sulphonic acid (64%), decomp. >310°, converted by aq. Br into 2:6-dibromo-4-fluoroaniline, m.p. 63—64°, which is also obtained from (II) by Br. 1:4:2- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{SO}_3\text{H}$, decomp. >325°, is similarly obtained and gives similarly 4:2:6:1- $\text{C}_6\text{H}_2\text{ClBr}_2\cdot\text{NH}_2$. 15% oleum converts (I) at 130—145° into 4-fluoroaniline-3-sulphonic acid (63%), decomp. >310° (Br_2 -derivative). 3:4:1- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}_2$ (similarly obtained), decomp. >310°, gives a Br_2 -derivative, decomp. >310°. Standard methods yield *sulphanil-p-fluoro*-, m.p. 163—164°, *-4'-fluoro-2'-sulpho*-, decomp. 285°, *-4'-fluoro-3'-sulpho*-, + H_2O , decomp. 260°, *-4'-chloro-2'-sulpho*-, + H_2O , decomp. 300°, and *-4'-fluoro-3'-sulpho*-, decomp. 310°, *-anilide*. R. S. C.

Preparation and resolution of α - β -diphenylethylenediamine (stilbenediamine). I. LEFSCHITZ and J. G. BOS (Rec. trav. chim., 1940, 59, 173—183; cf. Feist *et al.*, A., 1894, i, 196; 1896, i, 258).—1-Acetyl-2:4:5-triphenyl-4:5-dihydrogly-

oxaline and boiling aq. HCl give β -benzamido- α -acetamido- $\alpha\beta$ -diphenylethane, m.p. 251°, converted by conc. HCl-EtOH into r -(CHPh·NH₂)₂, b.p. 115°/5 mm., m.p. 83° (lit. 90–92°) [anhyd. dihydrochloride, m.p. 248° (decomp.) (cf. lit.)]; platinumchloride, decomp. 225°, resolved through the *l*-base *d*-tartrate (+2H₂O), [α]_D -11° in H₂O, and *d*-base *d*-tartrate, [α]_D +44° in H₂O, into the *l*- (I), [α]_D -87° in Et₂O, and *d*-base, [α]_D +86° in Et₂O, respectively. (I) gives the disalicyclidene derivative, m.p. 152°, [M]_D +417° in MeOH (cf. Pfeiffer *et al.*, A., 1938, II, 281).

A. T. P.

Behaviour of azo-compounds in solid-liquid systems in relation to the structure of the azo-group.—See A., 1940, I, 215.

Reactions of aliphatic diazo-compounds. I. E. JOLLES (Atti X Congr. Internaz. Chim., 1938, III, 220–225).—Mainly an account of work previously abstracted (A., 1938, II, 482). CH₂N₂ reacts vigorously with NPh·NBz, giving a compound, C₁₄H₁₂ON₂, m.p. 168°, which is probably β -benzoyl- α -phenyl- $\alpha\beta$ -methylenediazine. The compound from p -C₆H₄Me·N₂·CO·NH₂ and CH₂N₂ has m.p. 111.5° (cf. *loc. cit.*).

E. W. W.

Relation between absorption spectra and chemical constitution of dyes. XV. Influence of sulphonc acid groups in aminoazo-dyes. W. R. BRODE and D. R. EBERHART (J. Org. Chem., 1940, 5, 157–164).—Spectrophotometric study of 48 azo-dyes (as Na salts), obtained by coupling PhN₂Cl and SO₃H·C₆H₄·N₂Cl with α - and β -C₁₀H₇·NH₂ and their (SO₃H)₁-derivatives, leads to the following conclusions. Introduction of SO₃H has a definite effect on the absorption spectra, the nature being dependent on the position of both SO₃H and N·N (with respect to the NH₂-group). SO₃H in the C₁₀H₇ group usually produces a hypsochromic effect [max. for dyes from 1:2-NH₂·C₁₀H₆·SO₃H (I)]; only dyes from 1:8-NH₂·C₁₀H₆·SO₃H are bathochromic. SO₃H in the Ph group produces a bathochromic effect ($p > m > o$, except when the second component is a derivative of β -C₁₀H₇·NH₂, when the order is $o > p > m$). Change of solvent from neutral to acid causes a nearly complete reversal of frequency trend for dyes of type 1:4-NH₂·C₁₀H₆·N·NPh but not for those of type 1:2- (II) or 2:1-NH₂·C₁₀H₆·N·NPh. For the diazo-component, the frequency trend is reversed with change of solvent. The greatest decrease in frequency occurs with dyes from (I) (as second component) and from PhN₂Cl. Intensity of absorption follows the same general trends as frequency; the max. intensity is produced by 8-substitution in the C₁₀H₇ and p -substitution in the Ph. Dyes derived from (II) exhibit absorption curves in neutral solution in which the frequencies of the 3 principal max. are 2, 3, and 4 times that of a fundamental frequency of 310–330 fresnels.

H. B.

Catalytic hydrogenation of alicyclic ketazines.

II. Effect of ring-closure on velocity of hydrogenation of ketazines. V. I. EGOVA (J. Gen. Chem. Russ., 1939, 9, 1647–1651).—*cyclo*Hexyl Me ketone and N₂H₄·H₂O heated for 20 hr. at the b.p. yield the *azine*, m.p. 55–56.5°. The rate of hydrogen-

ation (Pt catalyst) of this is $>$ of the *azine* of COMe·C₆H₁₃· n ; the products are *s*-*di*-(α -cyclohexylethyl)-, b.p. 223°/210 mm., and *s*-*di*-(α -methylethyl)-hydrazine, b.p. 166°/8 mm. (*dihydrochlorides*), respectively.

R. T.

General method of preparation of α - and β -alkylphenylhydrazines. P. GRAMMATIKAKIS (Compt. rend., 1940, 210, 303–305; cf. A., 1939, II, 415; 1940, II, 131).—CHO·NPh·NH·CHO (I) with NaNH₂ in an inert solvent gives the Na derivative which with an alkyl halide, sulphate, or arylsulphonate in xylene at 140–150°, followed by hydrolysis with cold conc. HCl, gives a β -alkylphenylhydrazine (II) (alkyl = Me, Et, CH₂Ph, CHPhEt). Other diacyl analogues or organo-Mg derivatives of (I) react similarly. β -Acylphenylhydrazines give mixtures of α -alkylphenylhydrazine (III) and (II). NPh·NH·CH₂R (R = Ph, C₆H₄Me, C₆H₄·OMe) are easily oxidised to NPh·N·CHR, which are hydrolysed to RCHO. NNaPh·NH₂ (1 mol.) with alkyl halide or sulphate (1 mol.) in boiling (2–5 hr.) C₆H₆ or Et₂O gives (III) (alkyl = Me, Et, Pr^{*s*}, CH₂Ph).

J. L. D.

Associating effect of the hydrogen atom. VI. Acid hydrazides. H. T. HAYES and L. HUNTER (J.C.S., 1940, 332–336; cf. A., 1937, I, 513).—Mol. wt. determinations in C₁₀H₈, and experiments on solubility, show that the acid hydrazides, R·CO·NH·NHR' (I) and R·CO·NR''·NHR' (II) are associated. Association is due to H-bond formation between O of the acyl and, primarily, H of the adjacent NH (to a much smaller extent with H of the second NH). NHAc·NPh (III) and NHAc·NPhAc are highly associated (steep association–concn. curve), but NPhAc·NH₂ is almost non-associated. Progressive substitution of (III) supports the view that H of ·NPh may take part in H-bond formation; NHAc·NRPh (R = Me or Ph) gives a diminution in slope of curve, more marked with NPh·NRAc (R = Me or Ph), and greatest with NPhMe·NACMe. Mol. association of (I) is mainly by chain polymerides (cyclic are unlikely). Type (I) are sol. in H₂O and electron-donor solvents, but only sparingly in hydrocarbons; (II) are insol. in H₂O, but sol. in hydrocarbons. An explanation of the tautomerism R·CO·NH·NHR \rightleftharpoons OH·CR·N·NHR is suggested. *Acet*- $\alpha\beta$ -*di*-*o*-tolyl-, m.p. 107°, *p*-tolyl-, m.p. 120°, and *p*-chlorophenyl-hydrazide, m.p. 145°, $\alpha\beta$ -diacetylphenyl-*o*-tolylhydrazine, m.p. 91° (method: Smith *et al.*, J.C.S., 1908, 93, 1249), and *acet*- β -phenyl- α -*p*-tolylhydrazide, m.p. 140° (identical with the product of Jacobson *et al.*, A., 1899, 276) [reduced by Fe-AcOH to NH₂Ph and p -C₆H₄Me·NHAc], are described.

A. T. P.

Chemical constitution and reactivity. I. Effect of isomerism on the reactivity of diazo- and related azo-compounds. M. L. CROSSLEY (Atti X Congr. Internaz. Chim., 1938, III, 99–110).—C₆H₄Me·N₂Cl, which have the regular order of stability $p > o > m$, and C₆H₄Cl·N₂Cl (order of stability $o > p > m$) give, with 2:3:6-OH·C₁₀H₅(SO₃Na)₂, azo-dyes of an order of fastness $m > o > p$. It is suggested that the reactivity of any compound depends on the rate at which an “inactive” gives an

"active" phase. $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ show regular order of stability but $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ show $o > m > p$. E. W. W.

Reaction of diazo-compounds with primary amines containing salt-forming groups. I. Tautomeric triazens. II. General mechanism of the reaction. A. P. ERSCHOV and J. S. JOFFE (J. Gen. Chem. Russ., 1939, 9, 2211—2218, 2219—2231).—I. Substituted diazoaminobenzenes tautomerise in the following way in acid solution:

$\text{NR}\cdot\text{N}\cdot\text{NHR}' (a) \rightleftharpoons \text{NHR}\cdot\text{N}\cdot\text{NR}' (b)$. The following diazoaminobenzene derivatives are described (figures in parentheses are % of *b* form present in aq. solution): 2- (32), 3- (18), and 4-chloro-3'-sulpho- (25), 2:5:2'-trichloro-5'-sulpho- (19), 2:5-dichloro-2'- (59), 3'- (78), and 4'-carboxy- (67), 2:5-dichloro-2'- (46), 3'- (58), and 4'-sulpho- (50), 3'- (1) and 4'-sulpho-4-methyl- (1), 2:5-dichloro-2':5'- (9) and 3':5'-disulpho- (23.5), 2:5-dichloro-2'-carboxy-4'- (12) and 5'-sulpho- (40), 2:5-dichloro-2'-sulpho-4'- (20) and 5'-carboxy- (18). The sulpho-derivatives are as Na or, occasionally, K salts.

II. The following diazoaminobenzene derivatives are described: 2'-carboxy-4'- and 5'-sulpho-4-methyl-, 4-nitro-3'- and 4'-sulpho-, 4-nitro-2'-carboxy-4'-sulpho-. In general, substituted diazobenzenes react with substituted arylamines in alkaline solution thus: $\text{NR}\cdot\text{N}\cdot\text{OH} (I) + \text{NH}_2\text{R}' \rightarrow \text{NR}\cdot\text{N}\cdot\text{NHR}' (II) \rightleftharpoons \text{NHR}\cdot\text{N}\cdot\text{NR}' (III)$; $(II) + (I) \rightleftharpoons (\text{NR}\cdot\text{N})_2\text{NR}'$; $(III) + (I) \rightleftharpoons \text{NR}\cdot\text{N}\cdot\text{NR}\cdot\text{N}\cdot\text{NR}' \rightleftharpoons \text{NR}\cdot\text{N}\cdot\text{NHR} + \text{NR}'\cdot\text{N}\cdot\text{OH}$ [$\text{R} = 2:5\text{-C}_6\text{H}_3\text{Cl}_2$, $\text{R}' = o$ -, *m*-, and *p*- $\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ or $-\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, 2:4-, 2:5-, 3:6-, and 4:6- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{SO}_3\text{H}$, 2:5- $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2$; $\text{R} = p$ - $\text{C}_6\text{H}_4\text{Me}$, $\text{R}' = m$ - and *p*- $\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, 2:4- and 2:5- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{SO}_3\text{H}$; $\text{R} = p$ - $\text{C}_6\text{H}_4\cdot\text{NO}_2$, $\text{R}' = m$ - $\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, 2:4- and 2:5- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{SO}_3\text{H}$]. In aq. HCl solution the reactions are: $(II) + \text{HCl} \rightleftharpoons \text{RN}_2\text{Cl} + \text{NH}_2\text{R}'$; $(III) + \text{HCl} \rightleftharpoons \text{R}'\text{N}_2\text{Cl} + \text{NH}_2\text{R}$; $\text{RN}_2\text{Cl} + \text{NH}_2\text{R} \rightleftharpoons \text{NR}\cdot\text{N}\cdot\text{NHR} + \text{HCl}$; $\text{R}'\text{N}_2\text{Cl} + \text{NH}_2\text{R}' \rightleftharpoons \text{NR}'\cdot\text{N}\cdot\text{NHR}' + \text{HCl}$. R. T.

Hydrogen fluoride as a condensing agent. IX. Reactions of di- and tri-isobutene with phenol. J. H. SIMONS and S. ARCHER (J. Amer. Chem. Soc., 1940, 62, 451; cf. A., 1939, II, 428).—With a little 70% HF at 0°, PhOH and diisobutene give *p*-tert.-octylphenol, but with much HF in CCl_4 give *p*- $\text{C}_6\text{H}_4\text{Bu}^t\text{OH}$. "Triisobutene" gives only *p*- $\text{C}_6\text{H}_4\text{Bu}^t\text{OH}$. R. S. C.

4-Nitroso- and 4-amino-thymol. W. T. SUMERFORD and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1940, 29, 65—69).—Tautomeric change of 4-nitroso-thymol (I) ($\text{OH} = 1$) to thymoquinoneoxime can be effected by 0.15% aq. $\text{Ca}(\text{OH})_2$ or 20% aq. Na_2CO_3 ; 20% aq. NaHCO_3 is without effect. Hydrolysis of (I) with 7% HCl in presence of COMe_2 affords thymoquinone in 36% yield. (I) with H_2 and Pd-C or PtO₂ in EtOH-HCl (<1 equiv.) is quantitatively reduced to 4-aminothymol (II), which when diazotised and then added to agitated boiling H_2O affords thymoquinol in 43% yield. Colour changes during the oxidation of (II) are discussed. F. O. H.

Ditolyl series. VIII. A. ANGELETTI (Atti X Congr. Internaz. Chim., 1938, III, 26—31).—2-

Chloro-2'-amino-6:6'-dimethyldiphenyl (I) (A., 1932, 942) diazotised in HCl and heated at $>90^\circ$ (or treated with $\text{Cu}_2\text{Cl}_2\text{-HCl}$) gives 2:2'-dichloro-6:6'-dimethyldiphenyl, m.p. 119°. Similarly, in HBr, 2-bromo-2'-amino- (II) gives 2:2'-dibromo-6:6'-dimethyldiphenyl. In H_2SO_4 , (I) and (II), diazotised and heated, readily give 2-chloro-2'-hydroxy-, m.p. 65—66°, and 2-bromo-2'-hydroxy-6:6'-dimethyldiphenyl, m.p. 91—92°. 2-Iodo-2'-amino- similarly gives 2-iodo-2'-hydroxy-6:6'-dimethyldiphenyl, m.p. 58°. E. W. W.

Differentiation of phenols. I. Metallic derivatives of nitrosophenols. G. TRAVAGLI (Atti X Congr. Internaz. Chim., 1938, III, 372—375).—Certain phenols, e.g., α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, resorcinol (I), and phloroglucinol, give a characteristic ppt. with HNO_2 and a Co^{II} salt. (I) gives the compound, $(\text{C}_6\text{H}_4\text{O}_3\text{N})_3\text{Co}$ (structure suggested). E. W. W.

Aromatic stabilised ethylenic linkings. Mills-Nixon problem. R. T. ARNOLD and R. L. EVANS (J. Amer. Chem. Soc., 1940, 62, 556—558).—The following *pK* indicate that the ethylenic linkings are not stabilised by co-ordination: *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ 8.20 (29°); 5:1:2:4- $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{OH}$ 8.81 (28°), 8.90 (37°); 6-nitro-5-hydroxyhydrindene 8.96 (37°); 7-nitro-6-hydroxy-1:2:3:4-tetrahydronaphthalene (*Me ether*, m.p. 50—51.5°) 9.05 (37°); 3:1:4-8.57 (28°) and 4:1:3- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ 8.43 (28°). R. S. C.

Steric hindrance in ketone-naphthol condensations. Condensations of naphthols with cyclohexanone. J. B. NIEDERL, V. NIEDERL, and J. CHARNEY (J. Amer. Chem. Soc., 1940, 62, 322—323).—Condensation of ketones with naphthols parallels that with phenols (cf. A., 1939, II, 416). 1 mol. each of cyclohexanone (I) and α - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ with HCl at $<30^\circ$ give 80% of 1-4'-hydroxy-1'-naphthyl- Δ^1 -cyclohexene (II), m.p. 80°, but at 100° give 50% of 1:1-di-4'-hydroxy-1'-naphthylcyclohexane, m.p. 233° (dibenzate, m.p. 223°). The acetate, m.p. 94°, of (II) gives a dibromide (20%), m.p. 147°, titration of which with 0.01N-NaOH shows an equiv. wt. equal to half the mol. wt. owing to hydrolysis of Br. β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, (I), and HCl in AcOH at $<30^\circ$ give 20% of 1:2-tetramethylene-3:4- or -4:5-benzcoumarone, m.p. 66—68°. R. S. C.

Synthesis of 6-hydroxy-3:4-benzpyrene and 8-isopropyl-1:2-benzanthracene from 9:10-dihydrophenanthrene. L. F. FIESER and W. S. JOHNSON (J. Amer. Chem. Soc., 1940, 62, 575—577).—6-Keto-3:4:5:6-tetrahydrochrysene (I), $\text{CH}_2\text{Br}\cdot\text{CrO}_2\text{Me}$, and activated [conc. $\text{H}_2\text{SO}_4\text{-HNO}_3$ (trace); 100°] Zn in C_6H_6 give mixed acids [and much (I) recovered], which by esterification (HCl-MeOH), dehydration (distillation in vac.), and dehydrogenation (S; less well, Pd-C) give chrysene-6-acetic acid (II), m.p. 207—208°, and a small amount of a hydrocarbon. With HF, (II) gives 6-hydroxy-3:4-benzpyrene (57%), m.p. 195—196° (decomp.); no intermediate ketone could be found. γ -9:10-Dihydro-2-phenanthryl-butyric acid and HF give 8-keto-3:4:5:6:7:8-hexahydro-1:2-benzanthracene (89.5%), which with MgPr^tBr and subsequent dehydration and dehydrogenation (S; 205—250°) gives 8-isopropyl-1:2-

benzanthracene, m.p. 97—98° (*picrate*, m.p. 155.5—156.5°). M.p. are corr. R. S. C.

Exploration of methods for preparing stilbene derivatives. W. H. LINNELL and V. R. SHARMA (*Quart. J. Pharm.*, 1939, **12**, 263—270).—Attempts have been made to prepare 4:4'-dihydroxy- $\alpha\beta$ -diethylstilbene by removal of S from (? polymeric) p -OH-C₆H₄-CSEt or of N from the azine of p -OH-C₆H₄-COEt. p -OMe-C₆H₄-COEt and H₂S in dry EtOH-HCl give a cryst. compound (I), C₃₀H₃₆O₃S₂, m.p. 162°, which with Cu powder in boiling (CH₂OH)₂ yields a substance (II), C₄₀H₄₈O₄S₂, m.p. 115—116°. Cyclic structures are assigned to (I) and (II). p -Hydroxy- (III) and p -methoxy- (IV) -propiophenone-hydrazone when heated in vac. yield the respective azines, m.p. 167—168°, and 132—133° (V), which do not lose N when heated alone or with Mg or Li. (III) could not be oxidised by HgO in dry Et₂O; (IV) and HgO in light petroleum give a product converted by SO₂-Et₂O and then boiling H₂O into (V). p -OAc-C₆H₄-COEt does not give a pinacol with Mg and I in Et₂O-C₆H₆. F. H.

$\alpha\omega$ -Di- p -hydroxyphenylalkanes. E. M. RICHARDSON and E. E. REID (*J. Amer. Chem. Soc.*, 1940, **62**, 413—415).—Lower members of the series [CH₂]_n(C₆H₄-OH)₂ are bactericidal, but are too insol. for use. Partition coeffs. and regularities in m.p. are recorded. Anisoin gives (Clemmensen-Martin) (p -OMe-C₆H₄-CH₂)₂, m.p. 125.5—127°, and thence (p -OH-C₆H₄-CH₂)₂, m.p. 198—199°. p -OMe-C₆H₄-CH:CH-CO-C₆H₄-OMe- p (prep. from p -OMe-C₆H₄-CHO and p -OMe-C₆H₄-COMe), m.p. 100—101°, gives (Adams) $\alpha\gamma$ -di- p -anisyl-, m.p. 45—46°, and thence $\alpha\gamma$ -di- p -hydroxyphenyl-propane, m.p. 107—108°. p -OMe-C₆H₄-[CH₂]₃-CO₂H [prep. from PhOMe and (CH₂CO)₂O by way of the CO-acid] and SOCl₂ give the chloride, which with PhOMe gives a ketone, reduced (crude) to $\alpha\delta$ -di- p -anisyl- n -butane, m.p. 78—79°, which yields $\alpha\delta$ -di- p -hydroxyphenyl- n -butane, m.p. 158—159°. (p -OMe-C₆H₄-CH:CH)₂CO yields successively (p -OMe-C₆H₄-[CH₂]₂)₂CO, m.p. 55—55.2°, [CH₂]₃(C₆H₄-OMe- p)₂, and the derived (OH)₂-compound, m.p. 104—105°. $\alpha\zeta$ -Di- p -anisyl- n -hexane- $\alpha\zeta$ -dione [prep. from [CH₂]₄(COCl)₂, PhOMe, and AlCl₃ in CS₂], m.p. 145—146°, gives $\alpha\zeta$ -di- p -anisyl-, m.p. 70—71°, and thence $\alpha\zeta$ -di- p -hydroxyphenyl- n -hexane, m.p. 144.5—145.5°; $\alpha\kappa$ -di- p -anisyl- n -decane- $\alpha\kappa$ -dione, m.p. 119—119.5°, $\alpha\kappa$ -di- p -anisyl-, m.p. 69—70°, and $\alpha\kappa$ -di- p -hydroxyphenyl- n -decane, m.p. 138.5—139.5°, are similarly prepared. R. S. C.

Molecular rearrangements involving optically active radicals. VII. Rearrangement of optically active phenyl alkyl ethers. W. I. GILBERT and E. S. WALLIS (*J. Org. Chem.*, 1940, **5**, 184—191).—Mesityl (I) (from C₆H₂Me₃-SO₃H by fusion with KOH or, better, by cooling "Remington phenols") and *sec*-BuBr in EtOH-NaOEt give *dl*-mesityl *sec*-Bu ether (II), b.p. 72—73°/1 mm., decomp. when heated at atm. pressure; the corresponding *d*- (III), [α]_D²⁵ +6.97°, and *l*- (IV), [α]_D²⁰ -3.94°, -ethers are similarly prepared from (I) and *sec*-BuBr, [α]_D²⁰ -23.12° (cf. lit.) and [α]_D²² +12.71°, respectively (obtained from *sec*-BuOH, [α]_D²⁴ +11.67° and [α]_D²⁰ -10.84°, respectively). Rearrangement of (II) with ZnCl₂ in AcOH

at 115° in presence of *p*-cresol gives 3-*sec*-butyl-*p*-cresol (V) (small yield), C₄H₈, (I), *sec*-BuOAc, and unchanged materials. With conc. H₂SO₄ for ZnCl₂, a better yield of (V) results; (III) and (IV) similarly give *dl*-(V). The following reactions occur: (i) (II), (III), or (IV) \rightarrow (I) + C₄H₈; (ii) formation of p -C₆H₄Me-OBu-*sec*. (VI) from *p*-cresol and C₄H₈; (iii) rearrangement of (VI) to (V). Further evidence of intramol. reaction is obtained by treatment of PhOPr ^{β} + (VI) with AcOH-conc. H₂SO₄, when only *o*-C₆H₄Pr ^{β} -OH and (V) are produced. An intermol. mechanism cannot be used to explain retention of optical activity in the experiments previously described (A., 1934, 1097). H. B.

Migration and elimination of halogen from aromatic halogeno-compounds under the influence of catalysts. H. MEERWEIN, P. HOFMANN, and F. SCHILL (*J. pr. Chem.*, 1940, [ii], **59**, 266—283).—1:2:4-C₆H₃I(OMe)₂ (I) and BF₃.Et₂O at room temp. give 1:5:2:4-C₆H₂I₂(OMe)₂ (II) and *m*-C₆H₄(OMe)₂ (III). A similar reaction is observed using HCl, TiCl₄, or AlCl₃ in Et₂O, chlorocymene-sulphonic acid in AcOH, P₂O₅-C₆H₆ (slowly) at room temp., or HCO₂H at 96°. The reaction is reversible; (II) and (III) with CCl₃-CO₂H at 120° or, much less well, HCO₂H at 90—95° give (I). Migration of I is intermol. since (I) and PhOMe with CCl₃-CO₂H at 120° give (III) and *o*- + p -C₆H₄I-OMe; similarly (I)-PhOH-BF₃-CHCl₃ at room temp. give *o*-C₆H₄I-OH. 1:2:4-C₆H₃Br(OMe)₂ and BF₃ + BF₃.Et₂O give 1:5:2:4-C₆H₂Br₂(OMe)₂ and (III). 1:2:4-C₆H₃Cl(OMe)₂, BF₃.Et₂O, and BF₃ at 132—139° (sealed tube) give 1:5:2:4-C₆H₂Cl₂(OMe)₂ and (III). 1:2:4-C₆H₃(OMe)₃ and I-HgO-MeOH give 1-iodo-2:4:5-trimethoxybenzene (IV), m.p. 70—71°, converted by BF₃.Et₂O, CCl₃-CO₂H-CCl₄, or HCO₂H at 75°, or in boiling decahydronaphthalene alone, into 2:4:5:2':4':5'-hexamethoxydiphenyl (V). (IV) and Br-CCl₄ give 1:2:4:5-C₆H₂Br(OMe)₃, but Cl₂-CCl₄ give (V). Iodination of PhOMe or (III) could not be effected with (IV). Theoretical aspects are discussed; migration involves positive halogen. A. T. P.

Etherification and hydrolysis [of ethers] of nitrophenols. A. OLIVIERO (*Atti X Congr. Internaz. Chim.*, 1938, III, 258—263).—Boiling 10% KOH (24 hr.) hydrolyses *o*- and *p*-nitro-anisole and -phenetole only partly; the *m*-compounds are unchanged. Contrary to Cardwell *et al.* (*J.C.S.*, 1915, **107**, 256), 6-nitrohomoveratrole (I) is readily hydrolysed (with 2% KOH, 20% hydrolysis in 4 hr.). With boiling EtOH containing some aq. KOH, (I) gives 2:1:4:5-NO₂-C₆H₂Me(OEt)₂ (II). 4-Nitroveratrole (III) and EtOH give 3:3'-dimethoxy-4:4'-diethoxyazoxybenzene. With EtOH and some aq. NaOH, (III) gives 4:2:1-NO₂-C₆H₃(OMe).OEt (IV). In MeOH with aq. NaOH (best in sealed tube), the reactions are reversible, (II) and (IV) giving (I) and (III), respectively. Other examples of similar substitution reactions are given. E. W. W.

Chloroalkylation of phenolic ethers. I. Synthesis of methoxystyrenes. II. Syntheses of vinylanisole and of derivatives of methoxy- α -hydroxyethylbenzene. R. QUELET (*Bull. Soc.*

chim., 1940, [v], 7, 196—205, 205—215).—I. A mixture of PhOMe, (MeCHO)₃, and conc. HCl is saturated with HCl at ~5°, giving the very unstable OMe·C₆H₄·CHMeCl (I), which is transformed by C₅H₅N at ~115° into *p*-vinylanisole, b.p. 94°/17 mm., m.p. 2° (with a small proportion of the *o*-compound), which rapidly polymerises at room temp., and α -dianisylethane, b.p. 203—204°/10 mm., m.p. 72°, formed from (I) and unchanged PhOMe. The similar condensation with EtCHO is more difficult and is best effected in presence of H₃PO₄; the products are converted by C₅H₅N into anethole (with a small proportion of *o*-OMe·C₆H₄·CH:CHMe) and α -dianisylpropane, b.p. 197—200°/9 mm., m.p. 44°. PrⁿCHO more readily leads to *p*- Δ^4 -butenylanisole, b.p. 127°/16 mm., m.p. 19·5° (dibromide, m.p. 75—76°).

II. *o*-C₆H₄Me·OMe is converted by HCl and (MeCHO)₃ at 5—10° followed by C₅H₅N into 4-methoxy-3-methylstyrene, b.p. 105°/16 mm. (unstable dibromide), and α -4:4'-dimethoxy-3:3'-dimethyldiphenylethane; the crude, intermediate Cl-compound is transformed by NaOAc in AcOH into α -acetoxy- α -6-methoxy-*m*-tolylethane, b.p. 135—136°/10 mm., and by NaOMe or NaOEt into α -methoxy-, b.p. 116—117°/16 mm., or α -ethoxy-, b.p. 124—125°/16 mm., α -6-methoxy-*m*-tolylethane, respectively. Similarly, *m*-C₆H₄Me·OMe affords 4-methoxy-2-methylstyrene, b.p. 107°/16 mm.; the very unstable intermediate chloride yields α -acetoxy-, b.p. 128—129°/8 mm. (partial decomp.), α -methoxy-, b.p. 120°/16 mm., and α -ethoxy-, b.p. 128—129°/17 mm., α -5-methoxy-*o*-tolylethane. *p*-C₆H₄Me·OMe gives 2-methoxy-5-methylstyrene, b.p. 108°/17 mm. (dibromide, m.p. 61°), and α -acetoxy-, b.p. 130—131°/10 mm., α -methoxy-, b.p. 113°/16 mm., m.p. 43·5°, and α -ethoxy-, b.p. 119°/18 mm., α -4-methoxy-*m*-tolylethane. 4-Methoxy-2-methyl-5-isopropylstyrene, b.p. 122—123°/12 mm., 4-methoxy-2-methyl-5-isopropyl- α -methoxy-, b.p. 139—140°/16 mm., and α -ethoxy-, b.p. 132—133°/10 mm., *ethylbenzene* are described. H. W.

Preparation of $\alpha\beta$ -dichloroethylanisole; transition to α - and β -chloromethoxystyrenes. R. QUELET and J. ALLARD (Bull. Soc. chim., 1940, [v], 7, 215—227).—In part, a more extended account of work already reported (A., 1939, II, 59). $\alpha\beta$ -Dichloro- α -*p*-anisylethane is converted by KCN in aq. EtOH at 95° into 4:4'-dimethoxystilbene and β -chloro- α -ethoxy- α -*p*-anisylethane, b.p. 147°/16 mm., pyrolysed to EtOH and β -chloro- α -*p*-anisylethylene, b.p. 133—138°/16 mm., m.p. 32°, and transformed by NaOEt in EtOH at 100° into α -ethoxy- α -*p*-anisylethylene, b.p. 135—137°/16 mm., which is hydrogenated (Adams) to α -ethoxy- α -*p*-anisylethane, b.p. 114—115°/16 mm. *o*- and *p*-C₆H₄Me·OMe and 3:6:1-C₆H₃MePrⁿ·OMe give very poor yields of the corresponding $\alpha\beta$ -dichlorides, which are preferably obtained by addition of Cl₂ to the requisite methoxystyrenes. These compounds when treated with NaOEt or C₅H₅N give the following: α -, b.p. 145—150°/18 mm., and β -, b.p. 155—158°/18 mm., *-chloro- α -6-methoxy-*m*-tolylethylene*; α -, b.p. 135—137°/16 mm., and β -, b.p. 143—145°/16 mm., *-chloro- α -4-methoxy-*m*-tolylethylene*; α -, b.p. 158—160°/16 mm.,

and β -, b.p. 155—160°/16 mm., *-chloro- α -5-methoxy-4-isopropyl-*o*-tolylethylene*. H. W.

Steric hindrance in ketone-phenol condensations. Condensation of guaiacol with cyclic ketones. J. B. NIEDERL, V. NIEDERL, and J. GRUMER (J. Amer. Chem. Soc., 1940, 62, 320—322).—As anticipated (cf. A., 1939, II, 416), condensation of guaiacol (I) (1 mol.) with cyclohexanone, 4- or 3-methylcyclohexanone (0·5 mol.) by HCl in AcOH at room temp. gives 1:1-*di-4'-hydroxy-3'-methoxyphenyl-cyclohexane* (31%) (II), m.p. 174° (*phenylurethane*, m.p. 153°; *diacetate*, m.p. 157°; *dibenzoate*, m.p. 168°), 4- (10%), m.p. 165° (*phenylurethane*, m.p. 192°; *diacetate*, m.p. 136°; *dibenzoate*, m.p. 162°), or 3-methyl-cyclohexane (27%), m.p. 149° (*phenylurethane*, m.p. 187°; *diacetate*, m.p. 118°; *dibenzoate*, m.p. 171°), respectively, but with 2-methylcyclohexanone (1 mol.) gives 1-4'-*hydroxy-3'-methoxyphenyl-2-methyl- Δ^1 -cyclohexene* (~20%), an oil (oxyacetic acid derivative, m.p. 73°), with ~30% of its polymeride. With 48% HBr or HI (*d* 1·7), (II) gives (I) or *o*-C₆H₄(OH)₂, respectively. R. S. C.

Nitration of 6- and 7-methoxyacet-2-naphthalide. D. H. HEY and S. E. LAWTON (J.C.S., 1940, 384—387).—7:2-OMe·C₁₀H₆·NHAc and HNO₃ (*d* 1·42) in AcOH give 1- (I), m.p. 160°, and 8-nitro-7-methoxyacet-2-naphthalide (II), m.p. 229—230°. (I) and KOH-EtOH give 1:7:2-NO₂·C₁₀H₅(OMe)·NH₂ [Ac₂ derivative, m.p. 166°, also from (I)-Ac₂O] (cf. Fischer *et al.*, A., 1916, i, 718). (II) and NH₃-EtOH at 160°, then 200°, give 1:2:7-NO₂·C₁₀H₅(NH₂)₂, reduced by Sn-HCl-EtOH to 1:2:7-C₁₀H₅(NH₂)₃, converted by benzil in aq. EtOH into 3'-amino-2:3-diphenyl-5:6-benzquinoxaline, m.p. 215°. 6:2-OMe·C₁₀H₆·NHAc similarly affords 1- (III), m.p. 157°, and 5-nitro-6-methoxyacet-2-naphthalide (IV), m.p. 208—209°. (III) and KOH-EtOH give 1-nitro-6-methoxy-2-naphthylamine, m.p. 149—150°, also prepared from 1:2:6-NO₂·C₁₀H₅(OMe)₂ and NH₃-EtOH at 160°, then at 200°. (I) or (III) and nitrous fumes give N-NO-derivatives, m.p. 71° (decomp.) and 89° (decomp.), respectively, which in C₆H₆ do not evolve N₂, and regenerate (I) or (III), respectively. (II) and (IV) give normal NO-derivatives, m.p. 85° (decomp.) and 91° (decomp.), respectively, which with C₆H₆ give 8-nitro-7-, m.p. 128°, and 5-nitro-6-methoxy-2-phenyl-naphthalene, m.p. 178°, respectively, also obtained from 2:7- or 2:6-C₁₀H₆Ph·OMe, respectively, and HNO₃ (*d* 1·42) in AcOH. A. T. P.

Tin derivative of dithiopyrocatechol. H. P. BROWN and J. A. AUSTIN (J. Amer. Chem. Soc., 1940, 62, 673).—The red solid, supposed (Guha *et al.*, A., 1926, 398) to be *o*-SH·C₆H₄·SO₃H, is *Sn bisdithiopyrocatechol* (I) and is also obtained from *o*-C₆H₄(SH)₂ (II) by SnCl₄ or SnCl₂ + air (in absence of air? Sn^{II} dithiopyrocatechol is obtained) and as impurity in the prep. of (II) from *o*-C₆H₄(SO₂Cl)₂ by Sn-HCl. Conc. HCl converts (I) into (II), but subsequent addition of H₂O to the mixture regenerates (I). Similarly Sb, Zn, Fe^{III}, Pb, and Tl salts are formed from (II). R. S. C.

Hydrogen fluoride as a condensing agent. X. Rearrangements. J. H. SIMONS, S. ARCHER, and

D. I. RANDALL (J. Amer. Chem. Soc., 1940, **62**, 485—486).—PhBu^v and PhOH in HF at 0° partly exchange Bu^v, giving C₆H₅ and *p*-C₆H₄Bu^v·OH (10%). CPh₂·N·OH in AcOH—HF at 0° give 72% of NHPhBz. PhOAc and HF in C₅H₁₂ at 100° (not at 0°) give a poor yield of *p*-OH·C₆H₄·COMe. PhSO₃·C₆H₄Me-*p* and HF in ligroin at 100° give 10% of *Ph* 4-hydroxy-*m*-tolyl sulphone, m.p. 137—138°, also obtained by condensing PhSO₂Cl and *p*-C₆H₄Me·OMe by AlCl₃ in CS₂ to *Ph* 4-methoxy-*m*-tolyl sulphone, m.p. 137—138°, and hydrolysing this by AlCl₃ at 140—150°.

R. S. C.

Electrochemical method of introducing the thiocyno-radical into organic compounds. N. N. MELNIKOV, S. I. SKLJARENKO, and E. M. TSCHERKASOVA (J. Gen. Chem. Russ., 1939, **9**, 1819—1824).—When a current of 0.02 amp. per sq. cm. is passed through a system consisting of anolyte of org. compound + NH₄CNS in aq. EtOH and catholyte of 5% aq. NH₄CNS, CNS-compounds are obtained. Thus, PhOH gives *p*-OH·C₆H₄·CNS, *o*- or *m*-cresol gives 1:2:5- or (?) 1:3:5-C₆H₃Me(OH)·CNS, thymol affords 3:1:4:6-OH·C₆H₂MePr^β·CNS, carvacrol yields 4-thiocyano-2-methyl-5-isopropylphenol, m.p. 73.5—74.5°, 8-hydroxyquinoline gives 4-thiocyano-8-hydroxyquinoline, *o*- or *m*-toluidine gives, respectively, 5-thiocyano-*o*- and thiocyano-*m*-toluidine, and NHPhEt yields *p*-thiocyano-*N*-ethylaniline, m.p. 57—58°. 3-Thiocyano-*p*-cresol is very unstable, readily undergoing conversion into C₆H₄Me<O>S>CO.

R. T.

Sulphonation by means of sulphites. V. Formation of β-naphtholsulphonic acids. S. V. BOGDANOV [with O. J. NOVOSHILOVA] (J. Gen. Chem. Russ., 1939, **9**, 1846—1850).—At 85° the ratio Na₂SO₄:Na₂S₂O₆ = 2:1 when 0.5M-Na₂SO₃ is heated for 30 min. with MnO₂. In presence of β-naphtholsulphonic acids the oxidation is greatly accelerated; the yield of Na₂SO₄ rises in presence of acids not undergoing sulphonation [2:1:6-OH·C₁₀H₅(SO₃H)₂ and 2:1:3:6-OH·C₁₀H₄(SO₃H)₃], and falls with acids undergoing further sulphonation in these conditions [2:4-, 2:6-, and 2:7-OH·C₁₀H₆·SO₃H and 2:3:6-OH·C₁₀H₅(SO₃H)₂]. The yields of Na₂SO₄ + sulphonic acid and of Na₂S₂O₆ are const. in all cases, amounting to 76—79 and 21—24%, respectively. The ratio Na₂S₂O₆:sulphonic acid is variable.

R. T.

Condensation of phenylacetylene with methyl propyl ketone. N. M. MALENOK (J. Gen. Chem. Russ., 1939, **9**, 1947—1952).—CPh₂CH and COMePr condense (Grignard reaction) to α-phenyl-γ-methyl-Δ^α-hexinen-γ-ol, b.p. 116—116.5°/2 mm., which eliminates H₂O when boiled with Ac₂O, yielding α-phenyl-γ-methyl-Δ^α-hexin-Δ^γ-ene, b.p. 87.5—88°/1.5 mm. This with AcO₂H gives α-phenyl-γ-methyl-Δ^α-hexinene-γδ-diol, m.p. 75°, together with its γ-acetate, b.p. 143.5—144.5°/1.5 mm.

R. T.

Dehydration of tertiary alcohols containing the cyclohexane ring. W. A. MOSHER (J. Amer. Chem. Soc., 1940, **62**, 552—554).—The direction of loss of H₂O is determined by heating with I, continuously distilling off the H₂O and olefine formed, ozonising

the latter product, and determining the CH₂O, MeCHO, or COMe₂. 1-Methyl-, 1-ethyl-, and 1-*iso*-propyl-cyclohexanol and cyclohexyldimethylcarbinol give only 1-methyl-, >99% of 1-ethyl-, and ~95% of 1-*isopropyl*-cyclohexene, and about 50% each of *isopropylidene*- and *isopropenyl*-cyclohexane, respectively.

R. S. C.

Epimeric alcohols of the cyclohexane series. IV. Parachor as a criterion for cis-trans-isomerism. D. T. C. GILLESPIE, A. K. MACBETH, and J. A. MILLS (J.C.S., 1940, 280—282).—Parachors of 10 pairs of geometrical isomerides of the cyclohexane series are measured. With the exception of the menthones and menthyl acetates, the *trans*-isomeride shows the higher val.; the magnitude of the difference depends probably more on the chemical nature of the compound than on the relative size of substituent groups. Vals. are recorded for *l*- and *dl*-*iso*-menthone (cf. Read *et al.*, A., 1927, 772), *l*-, *dl*-neo-, *dl*-*iso*-, and *dl*-neo-*iso*-menthyl acetates; *cis*- and *trans*-*p*-menthane, -4-methyl- and -*isopropyl*-cyclohexylcarbinol (small differences in val.), -*di*-hydrocryptol, -*l*-3-methylcyclohexanol, -hexahydrocuminic ester, and -*di*hydrocryptyl acetate. Prep. of some of the compounds is described.

A. T. P.

Pyrenium compounds. XXXV. Oxidation of ketones with hydrogen peroxide. W. DILTHEY, M. INCKEL, and H. STEPHAN (J. pr. Chem., 1940, [ii], **59**, 219—237; cf. A., 1939, II, 224).—cyclo-Hexanone added to 30% H₂O₂ + 96% H₂SO₄ in Ac₂O at >20° gives the peroxide, (C₆H₁₀<O>O₂)₂, m.p. 132—133° (cf. Stoll *et al.*, A., 1930, 602); excess of H₂SO₄ in place of Ac₂O affords polymerised ε-hydroxyhexoic acid (derived hydrazide, m.p. 117°) (cf. van Natta *et al.*, A., 1934, 392). Similarly prepared are the dimeric 4-, m.p. 71—72°, and 2-methylcyclohexanone peroxide, m.p. 106—107°, and cyclopentanone peroxide, trimeric, m.p. 172° (decomp.), and dimeric, m.p. 105° (cf. Milas *et al.*, A., 1939, II, 503) (excess of H₂SO₄ gives δ-hydroxyvaleric acid). 3-Methylcyclopentanone and CO(CH₂Ph)₂ afford peroxides in small yield. COMe₂ and CPhMe give dimeric peroxides, m.p. 132° (cf. Baeyer *et al.*, A., 1900, i, 328) and new m.p. 185—186°, respectively. The dimeric peroxides, m.p. 102—103°, and m.p. 47—48°, of CH₂Ph·CH₂·COMe and CPr^α₂, respectively, are prepared. COMeEt and COBu^β₂ give explosive oils (mainly trimeric, with some dimeric peroxide); COEt₂ and COMePr give no stable peroxide. CPh₂ affords PhOBz, formed probably by rearrangement of peroxide (cf. dimeric peroxide, Marvel *et al.*, A., 1938, II, 327). *p*-OMe·C₆H₄·CHO or *o*-OH·C₆H₄·CHO gives decomp. products only, and *o*- or *m*-NO₂·C₆H₄·CHO affords *o*- or *m*-NO₂·C₆H₄·CO₂H, respectively. No peroxide is obtained from menthone; mechanisms of oxidation are discussed (cf. Baeyer, A., 1900, i, 132): ε-hydroxy-β^γ-dimethyloctioic acid lactone or Et ester (*loc. cit.*) and MgPhBr give αα-*diphenyl*-γγ-*dimethyloctane*-αα'-diol, m.p. 91°. *d*-*iso*Menthone gives no peroxide.

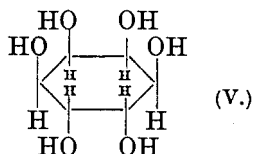
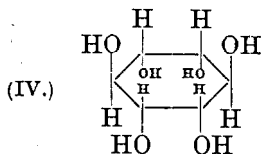
A. T. P.

Enediols. III. αβ-Dimesitylacetylene glycol. R. C. FUSON, C. H. MCKEEVER, and J. CORSE (J.

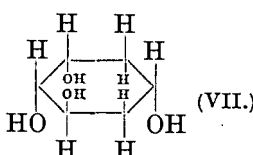
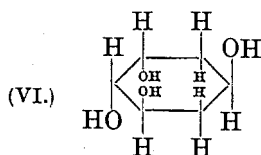
Amer. Chem. Soc., 1940, **62**, 600—602).—Mg + MgI₂ converts MCOCl (here and below M = mesityl) or (MCO)₂ in Et₂O-C₆H₆-N₂ into αβ-dihydroxy-αβ-dimesitylethylene (I) (cf. A., 1939, II, 260), also obtained by hydrogenating (MCO)₂ in MeOH or light petroleum. The diol gives *diacetates*, m.p. 218° and 164—165°, and *dibenzoates*, m.p. 235° (cf. Thompson, A., 1939, II, 316) and 188.5—189.5°, the proportions in which they are formed varying according to the method of prep. and solvent (for hydrogenation). Ketone to OH·CHM·COM is effected by HCl in boiling MeOH, and conversion into (MCO)₂ by air or oxidising agents.

R. S. C.

Constitution of conduritol and cyclohexane-tetraols. G. DANGSCHAT and H. O. L. FISCHER (Naturwiss., 1939, **27**, 756—757; cf. A., 1937, II, 382).—Conduritol (I) (cf. Kubler, A., 1909, i, 40) and COMe₂-HCl give the 4:5-CMe₂ ether, m.p. 100—101°, the diacetate, m.p. 79°, of which with neutral KMnO₄ gives 1:2:4:5-tetrahydroxy-3:6-diacetoxycyclohexane 4:5-CMe₂ ether (II). (II) and Pb(OAc)₄-C₆H₆, then EtCO₃H, give (after hydrolysis) mucic acid. The *tetra-acetate*, b.p. 165°/0.6 mm., of (I) is converted by KMnO₄ into 1:2-dihydroxy-3:4:5:6-tetra-acetoxycyclohexane (III), and thence by Pb(OAc)₄ into tetra-acetylmucic dialdehyde, which is oxidised (EtCO₃H) and hydrolysed to mucic acid. Acetylation of (II), mild hydrolysis (loss of CMe₂), and oxidation [Pb(OAc)₄] gives *tetra-acetylallomucic dialdehyde*, decomp. 164°, converted by EtCO₃H into tetra-acetylallomucic acid, decomp. 228°, and thence into *allomucic acid*. (III) is hydrolysed to *muconositol* (IV), decomp. 285—290°, and (II) affords *alloinositol* (V), decomp. 270—275° (cf. Posternak, A., 1936, 1376). (I) and H₂-Pd



give the H₂-derivative, m.p. 204° [CMe₂ ether, m.p. 80°, best prepared by reduction of the CMe₂ ether of (I)]. 3:4:5-Trihydroxycyclohexanone 4:5-CMe₂ ether (A., 1932, 849) is reduced by H₂-Ni or Al(OPrⁱ)₃ to (after removal of CMe₂) isomeric [as (VI) and (VII)] cyclohexane-1:3:4:5-tetraols, m.p. 208°, [α]_D -8.3° in H₂O, and m.p. 151°, [α]_D -61.0° in H₂O, respectively.



A. T. P.

Reduction of α-amino-esters to alkamines in presence of Raney nickel. G. OVAKIMIAN, M. KUNA, and P. A. LEVENE (J. Amer. Chem. Soc., 1940, **62**, 676—677).—Hydrogenation (Raney Ni; cf. de Benneville *et al.*, A., 1940, II, 186) of *l*-leucine ester and *l*-NHPh·CH₂·CO₂Et (I) gives <40 and 60%,

respectively, of *l*-β-aminoisohexyl and *l*-β-anilinoethyl alcohol, [α]_D²⁵ +1.9° and -5.61° in MeOH, respectively. Under other conditions (I) yields β-hydroxy-α-cyclohexylethylamine. With these and other NH₂-esters formation of piperazines or *sec*-amines occurs under certain conditions.

R. S. C.

Ephedrine. III. Di-β-methylamino-α-hydroxypropylbenzenes. S. D. WILSON and C. T. CHANG (J. Amer. Chem. Soc., 1940, **62**, 287—288; cf. A., 1935, 209).—*p*-C₆H₄(COEt)₂ and Br in AcOH at 100° give the αα'-Br₂-compound, m.p. 109—110°, and thence (NH₂Me; C₆H₆; room temp. etc.) *p*-di-α-methylaminopropionylbenzene *dihydrochloride*, decomp. >320°, reduced by H₂-PtO₂ in 95% EtOH to *p*-di-β-methylamino-α-hydroxy-*n*-propylbenzene *dihydrochloride*, m.p. 285—287° (corresponding sulphate, decomp. >320°, mandelate, m.p. 214°, and tartrate, m.p. 167—168°; free base, amorphous). *m*-C₆H₄(COEt)₂ [prep. from *m*-C₆H₄(CO·NET₂)₂ by MgEtBr improved to give 35—40% yield] gives similarly oily *m*-C₆H₄[CH(OH)·CHMe·NHMe]₂·2HCl; other salts and intermediates are also oils, but the free base is an amorphous solid.

R. S. C.

Diphenylmethane series. L. MASCARELLI and M. PIRONA (Atti X Congr. Internaz. Chim., 1938, III, 249—250).—The prep. of *o*-C₆H₄Me·CH₂Ph (I) is improved; *o*-C₆H₄MeBz is reduced to *o*-C₆H₄Me·CHPh·OH, and this (Clemmensen) to (I). *o*-C₆H₄Me·MgBr and *o*-NO₂·C₆H₄·CHO, give *2-nitro-2-methylbenzhydrol*, m.p. 93—96°.

E. W. W.

Constitution of cholesterol. Reactions with di- and tri-chloroacetic acids. F. PIRRONE (Atti X Congr. Internaz. Chim., 1938, III, 283—289).—Cholesterol (I) with CCl₃·CO₂H at room temp. is unchanged (cf. Montignie, A., 1929, 1292), but at 100° it gives *cholesteryl trichloroacetate*, m.p. 148—149° (Br₁-derivative, m.p. 78—81°), hydrolysed to (I). At 140°, amorphous products are obtained. In C₆H₆, some *isocholesterol* is formed. With CHCl₂·CO₂H at 140° or in C₆H₆, (I) gives *cholesteryl dichloroacetate*, m.p. 107—107.5° (*dibromide*, m.p. 55—57°), hydrolysed to (I).

E. W. W.

Constitution of cholesterol. Oxidation by peracetic acid. F. PIRRONE (Atti X Congr. Internaz. Chim., 1938, III, 290; cf. A., 1939, II, 504).—Cholesterol and AcO₂H give a *cholestanetriol diacetate*, m.p. 164—165°, a *cholestanetriol*, m.p. 217—218°, and a *hydroxycholestanol*, m.p. 121—122°.

E. W. W.

Isomerisation of cholesterol α-oxide. M. I. USCHAKOV and O. S. MADAEVA (J. Gen. Chem. Russ., 1939, **9**, 1690—1692).—Cholesterol α-oxide (I) and MgI₂ in boiling C₆H₆ gradually yield cholesterol. With MgBr₂ in Et₂O (5 hr. at 100°), (I) affords a substance, C₂₇H₄₄O, m.p. 105.5—106.2°. When a solution of (I) in dioxan is heated with 2N-H₂SO₄ (24 hr. at the b.p.), *cholestane-3:5:6-triol* is obtained.

R. T.

Brassicasterol. II. Degradation by ozone. E. FERNHOLZ and H. E. STAVELY (J. Amer. Chem. Soc., 1940, **62**, 428—430).—O₃ converts brassicasteryl acetate (as *dibromide*) in CHCl₃ into (after debromination) β-3-hydroxybismorcholenic acid; the

acetate and O_3 in AcOH give partly racemised $CHMePr^{\beta}\cdot CHO$ (semicarbazone, m.p. 119° , $[\alpha]_D^{25} -39.4 \pm 2^{\circ}$ in EtOH). Brassicasterol is thus $C_{28}H_{46}O$ (cf. A., 1939, II, 112) and is probably 7:8-dihydro-ergosterol. *Brassicasteryl acetate 22:23-dibromide* (prep. from the tetrabromide by NaI), m.p. $236-238^{\circ}$, and *ergostanyl 3:5-dinitrobenzoate*, m.p. $202-203^{\circ}$, $[\alpha]_D^{25} +14^{\circ}$ in $CHCl_3$, are described. R. S. C.

Sterols. LXXXIX. Reactions of ψ -sarsapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 521-525).—The following and known reactions support the view that ψ -sarsapogenin (I) contains the grouping $\cdot CMe\cdot C(OH)\cdot [CH_2]_2\cdot CHMe\cdot CH_2\cdot OH$ ($= R$) and its H_2 -derivative (II) contains the grouping $\cdot CMe\cdot CR\cdot CH\cdot CH_2\cdot CH$ in which the side-chain is reduced. (I) is very readily oxidised by SeO_2 and reacts with Br. Neither (I) nor its acetate (III) reacts with semicarbazide. CrO_3 in $\sim 90\%$ AcOH at 100° oxidises (III) to 3-acetoxy α -etibilanic acid (IV) and a small amount of a neutral substance, hydrolysed to an acid, $C_{22}H_{34}O_4$, m.p. $284-287^{\circ}$, but at room temp. (1 hr.) some 3(β)-acetoxy- $\Delta^{16:17}$ -pregnen-20-one (V), m.p. $144-146^{\circ}$ [semicarbazone, m.p. $250-252^{\circ}$; further oxidised to (IV) by CrO_3 at room temp. (16 hr.)], is also obtained. KOH-EtOH hydrolyses (V) to $\Delta^{16:17}$ -pregnen-3(β)-ol-20-one, +EtOH, m.p. $207-209^{\circ}$ [semicarbazone, m.p. 240° (decomp.)], oxidised by CrO_3 in 90% AcOH at room temp. to $\Delta^{16:17}$ -pregnene-3:20-dione (VI). (V) is reduced by Na-EtOH to pregnene-3(β):20(α)-diol, or by H_2 -PtO₂ at 3 atm. in abs. EtOH to an oil, yielding with CrO_3 either pregnane-3:20-dione or 3(β)-acetoxypregnan-20-one. Hydrogenation (PtO₂; 3 atm.; AcOH, EtOH, or EtOH-HCl) and subsequent hydrolysis (KOH-EtOH) converts (I) into (II), m.p. $168-170^{\circ}$ (*di-p-nitrobenzoate*, m.p. $196-197.5^{\circ}$; stable to SeO_2 ; absorbs Br slowly), the *diacetate*, m.p. $95-97^{\circ}$ [obtained also by reduction of (III)], of which with CrO_3 -AcOH at 90° gives (IV) and at room temp. also (V). CrO_3 in AcOH at $15-18^{\circ}$ oxidises (II) to (VI) and a (CO)₂-acid, $C_{22}H_{42}O_4$, m.p. $233-236^{\circ}$ [*disemicarbazone*, m.p. 209° (decomp.)]; *Me ester*, m.p. $85-87^{\circ}$, further oxidised at 25° to (VI). R. S. C.

Sterols. LXXXVIII. Pregnanediols from sarsapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 518-520).—Sarsapogenin acetate with Ac_2O , (EtCO)₂O, (Pr^oCO)₂O, or, less well, (CH₃CO)₂O [not o -C₆H₄(CO)₂O] at $195-200^{\circ}$ gives [after hydrolysis (EtOH-KOH)] $\sim 70\%$ of ψ -sarsapogenin (I) (cf. A., 1940, II, 84) (*di-p-nitrobenzoate*, m.p. $156.5-159^{\circ}$) and the C_{22} OH-lactone. CrO_3 in 80% AcOH at room temp. converts (I) into $\Delta^{16:17}$ -pregnene-3:20-dione ($50-70\%$), m.p. $200-202^{\circ}$ (lit. 196°) [*disemicarbazone*, m.p. 310° (decomp.)]; with some 3-keto α -etibilanic acid, reduced by Na-EtOH to pregnane-3(α):20(α)-diol, by H_2 -PtO₂ at 3 atm. in abs. EtOH to pregnane-3(α):20(β)-, -3(β):20(β)-, and -3(β):20(α)-diols, and by H_2 -Pd-BaSO₄ in abs. EtOH to pregnane-3:20-dione [*disemicarbazone*, m.p. 244° (decomp.)]. The presence of Me at C₍₂₁₎ and of OH

at C₍₃₎ in sarsapogenin and tigogenin is thus proved. R. S. C.

Sterols. XC. Oxidation products of sarsapogenin. *Pregnane-3:16:20-triol*. R. E. MARKER, E. ROHRMANN, H. M. CROOKS, E. L. WITTLE, E. M. JONES, and D. L. TURNER (J. Amer. Chem. Soc., 1940, 62, 525-527).—Sarsapogenin acetate, $K_2S_2O_8$, and a little H_2SO_4 in boiling 90% AcOH give an ester $\cdot CMe\cdot CHR\cdot CH\cdot CH_2\cdot CH\cdot OAc$ ($R = CHMe\cdot O\cdot CO\cdot [CH_2]_2\cdot CHMe\cdot CH_2\cdot OAc$), hydrolysed by KOH-EtOH to *pregnane-3(β):16:20-triol* ($20-40\%$), m.p. $223-226^{\circ}$ (*tribenzoate*, m.p. $185-187^{\circ}$; *triacetate*, m.p. $108-111^{\circ}$), which with CrO_3 in 90% AcOH at room temp. gives an oil, reduced by Na-EtOH to pregnane-3(α):20(α)-diol. *epiSarsapogenin acetate* gives similarly *pregnane-3(α):16:20-triol*, m.p. $206-207^{\circ}$ (*tribenzoate*, m.p. $153-155^{\circ}$), and acids. R. S. C.

***p*-cycloHexylphenoxyacetic acid and its derivatives.** D. BODROUX and A. CHATENET (Bull. Soc. chim., 1940, [v], 7, 191-195).—An account of work previously reviewed (A., 1938, II, 409). H. W.

Condensations brought about by bases. IX. Relationship between the Claisen and Perkin types of condensations. C. R. HAUSER and D. S. BRESLOW (J. Amer. Chem. Soc., 1940, 62, 593-597; cf. A., 1940, II, 91).—The mechanisms of the Claisen and Perkin condensations are discussed. Pr^oCO_2Et (I), PhCHO, and NaOEt in Et₂O give only $CH_2Ph\cdot OH$ (II) and BzOH (cf. Müller *et al.*, A., 1935, 344). $OH\cdot CHPh\cdot CMe_2\cdot CO_2Et$ (modified prep.), m.p. $38.5-39^{\circ}$, with NaOEt-Et₂O gives (I) and PhCHO [whence (II) and BzOH], and with $CNaPh_3$ gives (cf. A., 1939, II, 262) PhCHO [as (II) and BzOH] and $Pr^oCO\cdot CMe_2\cdot CO_2Et$. R. S. C.

Alkaline decomposition of substituted aliphatic β -hydroxy-acids. [IV.] α -Alkyl-acids. D. IVANOV (Atti X Congr. Internaz. Chim., 1938, III, 209-212).—Esters of type $OH\cdot CR'_2\cdot CHR\cdot CO_2Et$, viz., $OH\cdot CPh_2\cdot CHEt\cdot CO_2Et$, $CH_2Ph\cdot CPh(OH)\cdot CHEt\cdot CO_2Et$, and $OH\cdot CPhEt\cdot CHEt\cdot CO_2Et$, when heated with alkali (cf. A., 1933, 807) give $90-99\%$ of the theoretical yield of the ketone COR'_2 . β -Hydroxy- β -phenyl- α -dimethylvaleric acid, m.p. 101.5° , does not undergo this reaction, nor do the acids $OH\cdot CHPh\cdot CHEt\cdot CO_2H$, $OH\cdot CHPh\cdot CMe_2\cdot CO_2H$, or $OH\cdot [CMe_2]_2\cdot CO_2H$, or the esters $OH\cdot CHMe\cdot CMe_2\cdot CO_2Et$, $OH\cdot CHPr^o\cdot CHMe\cdot CO_2Et$, $OH\cdot CMe_2\cdot CHMe\cdot CO_2Et$, $OH\cdot CMe_2\cdot CHEt\cdot CO_2Et$, or $OH\cdot CPr_2\cdot CMe_2\cdot CO_2Et$. E. W. W.

Separation of *cis*- and *trans*-acids of the acrylic series. [Nitrocinnamic acids.] M. A. VERCILLO (Atti X Congr. Internaz. Chim., 1938, III, 375-379).—Separation of *cis*- and *trans*-isomerides of *o*-, *m*-, and *p*-nitrocinnamic acids by formation of Me esters, or by partial salt-formation using Li_2CO_3 (half theoretical quantity), is not very successful. Better results are obtained by fractional pptn. of the acids by AcOH or HCl from solutions of their Li salts; the *trans*-isomerides are the first pptd. E. W. W.

Synthesis of polycyclic compounds. II. Reformatsky reaction with 9-methyl-1:2-benzanthrone-10. B. M. MICHAÏLOV and N. G. TSCHERNOVA (J. Gen. Chem. Russ., 1939, 9, 2171—2172).—9-Methyl-1:2-benzanthrone-10, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and $\text{Zn}\cdot\text{Cu}$ in C_6H_6 yield 9-methyl-1:2-benz-10-anthranyl-acetic acid, m.p. 200—227° (decomp.) [*Et* ester, m.p. 81.6—83°; *amide*, m.p. 270—272° (decomp.)], converted into 9:10-dimethyl-1:2-benzanthracene by heating at the m.p., or with SnCl_2 . R. T.

Synthesis of 3:5-difluoro- and 5-iodo-3-fluoro-*dl*-tyrosine. J. ENGLISH, jun., J. F. MEAD, and C. NIEMANN (J. Amer. Chem. Soc., 1940, 62, 350—354).— $\text{o}\cdot\text{C}_6\text{H}_4\cdot\text{F}\cdot\text{OMe}$ (I) (prep. in 30.8% yield from $\text{o}\cdot\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ by way of the diazonium fluoroborate), b.p. 69—70°/26 mm., gives (cf. Schiemann and Miao, A., 1933, 1156) successively 4:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{F}\cdot\text{OMe}$ (39—40%), m.p. 104.5°, (by $\text{SnCl}_2\cdot\text{HCl}$) 4:3:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{F}\cdot\text{NH}_2$ (65—75%), m.p. 82°, (diazo-reaction) 2-fluoro-4-cyanoanisole (46%), m.p. 96.5°, b.p. 96—98°/1.5 mm., (by $\text{SnCl}_2\cdot\text{HCl}\cdot\text{Et}_2\text{O}$) 4:3:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{F}\cdot\text{CHO}$ (II) (63%), m.p. 29—30°, b.p. 93°/4.5 mm. [obtained less well from (I) by $\text{Zn}(\text{CN})_2\cdot\text{AlCl}_3\cdot\text{HCl}\cdot\text{C}_6\text{H}_6$ at 40—50°], 2-phenyl-4-3'-fluoro-4'-methoxybenzylideneoxazol-5-one, m.p. 207° (corr.), and 3-fluoro-*dl*-tyrosine (49%), decomp. 275—278° (rapid heating). $\text{I}\cdot\text{KI}$ in $\text{Sn}\cdot\text{aq. NH}_3$ then gives 5-iodo-3-fluoro-*dl*-tyrosine (47%), m.p. 192° (decomp.). $\text{Ac}_2\text{O}\cdot\text{AlCl}_3$ in CS_2 converts (I) into 3-fluoro-4-methoxyacetophenone (70—80%), m.p. 92° {5- NO_2 -derivative (III) [prep. by HNO_3 (*d* 1.5) in H_2SO_4 at -10°], b.p. 144—147°/4 mm. [*phenylhydrazone*, m.p. 160—161° (decomp.)], oxidised by $\text{KMnO}_4\cdot\text{KOH}$ at 80° to 4:3:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{F}\cdot\text{CO}_2\text{H}$ (IV) (70%), m.p. 208—210°. With $\text{H}_2\text{SO}_4\cdot\text{HNO}_3$ (*d* 1.5) at -10° (II) gives its 5- NO_2 -derivative (V) (55%), m.p. 57—58° (*oxime*, m.p. 138—139°). HNO_3 (*d* 1.5) and (IV) at -5° to 0° give 3-fluoro-5-nitro-*p*-anisic acid (57%), m.p. 166° [also obtained from (III) or (V) by KMnO_4 at 100°], the *Me* ester, m.p. 50°, b.p. 128—131°/3 mm., of which is hydrogenated (PtO_2) in MeOH to *Me* 3-fluoro-5-amino-*p*-anisate (90%), m.p. 55°. Distillation of the derived diazonium fluoroborate and subsequent hydrolysis gives 3:5-difluoro-*p*-anisic acid (VI) (28%), m.p. 162°, the crude acid chloride, m.p. 15—20°, of which is hydrogenated ($\text{Pd}\cdot\text{BaSO}_4$; xylene; quinoline-S) to 4:3:5:1- $\text{OMe}\cdot\text{C}_6\text{H}_2\cdot\text{F}_2\cdot\text{CHO}$, a liquid, which yields 52% of 2-phenyl-4-3':5'-difluoro-4'-methoxybenzylideneoxazol-5-one, m.p. 165—169° (decomp.), and thence (by $\text{NaOH}\cdot\text{EtOH}$) 3:5-difluoro- α -benzamido-4-methoxycinnamic acid, m.p. 200—201°, or (by red $\text{P}\cdot\text{HI}\cdot\text{Ac}_2\text{O}$) 3:5-difluoro-*dl*-tyrosine (62%), m.p. 263—265° (decomp.). Hydrogenation ($\text{PtO}_2\cdot\text{FeCl}_2$; EtOH ; 3—4 atm.) of (V) gives 3-fluoro-5-amino-4-methoxybenzyl alcohol, m.p. 55°, b.p. 141°/2 mm. [also obtained from (V) by $\text{Al}(\text{OPr}^i)_3\cdot\text{Pr}^i\text{OH}$], which gives no diazonium fluoroborate. 3-Fluoro-5-amino-4-methoxyacetophenone [prep. by hydrogenation of (III)], b.p. 138°/2.5 mm. (*hydrochloride*, decomp. 160—175°), also gives no diazonium fluoroborate. (VI) could not be obtained from the 3:5-tetrazonium fluoroborate of 3:5:4:1- $(\text{NH}_2)_2\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CO}_2\text{Me}$. 4-Nitro-2:6-diamino-

phenol, m.p. 169° (decomp.), obtained (45%) from picric acid by $\text{H}_2\text{S}\cdot\text{NH}_3\cdot\text{H}_2\text{O}$ at 75°, gives the Ac_2 derivative, m.p. 235° (decomp.), and thence 4-nitro-2:6-diaminoanisole, m.p. 180—181° (Ac_2 derivative, m.p. 211°); the derived tetrazonium fluoroborate decomposes explosively. Decomp. of 5:3:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_2\cdot\text{F}(\text{OMe})\cdot\text{N}_2\cdot\text{BF}_4$ gives only 10% of 2:6-difluoro-4-nitroanisole, m.p. 35°. R. S. C.

Photochemical inter-reactions of oxalyl chloride and phosgene with cyclohexane. M. S. KHASRASH and H. C. BROWN (J. Amer. Chem. Soc., 1940, 62, 454).—Photolysis (W lamp) of $(\text{COCl})_2$ or COCl_2 in cyclohexane gives cyclohexanecarboxyl chloride with $\text{HCl} + \text{CO}$ or HCl , respectively, indicating decomp. of $(\text{COCl})_2$ into $\text{CO}\cdot\text{COCl} + \text{Cl}$ (or 2COCl) and of COCl_2 into $\text{COCl} + \text{Cl}$. R. S. C.

Molecular compounds in binary systems: benzoic acid and nitro-, hydroxy-, and amino-benzoic acids.—See A., 1940, I, 215.

Azactones. II. Azactone formation in glacial and in aqueous acetic acid and preparation of α -benzamidoacrotic acid azlactone II. H. E. CARTER and C. M. STEVENS (J. Biol. Chem., 1940, 133, 117—128; cf. A., 1939, II, 423).—*N*-Benzoyl-*O*-methyl-*dl*-allothreonine (I) with Ac_2O yields α -benzamidoacrotic acid azlactone II (II), m.p. 144—145°, converted by $\text{C}_5\text{H}_5\text{N}$ into the isomeric azlactone I (III), m.p. 95—96° (*loc. cit.*). Hydrolysis (0.5*N*- HCl) of (II) yields α -benzamidoacrotic acid II, m.p. 195—198° (IV); acid I (*loc. cit.*) has m.p. 193—195° (V). With aq. $\text{AcOH}\cdot\text{NaOAc}$, (I) or (V) yields a mixture of (II) and (III), also obtained in much lower yield in absence of NaOAc . In AcOH with a little Ac_2O , the rate of azlactonisation is greatly increased by NaOAc . The rate of azlactonisation of benzoyl-*l*-p-methoxyphenylalanine (VI) in AcOH is increased by additions of NaOAc or Ac_2O ; (VI) is thereby racemised [and also by Ac_2O and by the azlactones of benzoyl-*dl*-p-methoxyphenylalanine (*amilide*, m.p. 207—209°), -*dl*-phenylalanine, and -*dl*-alanine in AcOH]. It is suggested that the racemisation of an acylated amino-acid by excess of Ac_2O in either aq. AcOH or AcOH depends on the formation of azlactone as an intermediate. NaOAc increases the rate of racemisation by increasing the rate of azlactonisation. (II) and (III) are *cis-trans* isomerides. J. D. R.

Mechanism of benzoyloxylation of ethylenes by the iodine-silver benzoate complex. C. PRÉVOST (Atti X Congr. Internaz. Chim., 1938, III, 318—324).—A review (cf. A., 1934, 989; 1935, 728; 1937, II, 289; etc.). The formation of $\text{OBz}\cdot\text{CHR}\cdot\text{CHR}'\cdot\text{OBz}$ from $\text{CHR}\cdot\text{CHR}'$ and $\text{Ag}(\text{OBz})_2\text{Hal}$ is considered to involve the intermediate compound $\text{OBz}\cdot\text{CHR}\cdot\text{CHR}'\cdot\text{Hal}$, which under certain conditions may be isolated. E. W. W.

Auto-metalation with sodium *m*-tolyl. H. GILMAN and H. A. PACEVITZ (J. Amer. Chem. Soc., 1940, 62, 673—674).—*m*- $\text{C}_6\text{H}_4\text{MeCl}$ and Na in light petroleum at 35—40° followed by solid CO_2 give *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$, but, if the mixture is boiled, only ~5% of $\text{CH}_3\text{Ph}\cdot\text{CO}_2\text{H}$ (similarly formed from *p*- $\text{C}_6\text{H}_4\text{MeCl}$ in 65% yield) is obtained. R. S. C.

Composition and structure of chromium compounds of azo-dyes from salicylic acid. K. BRASS and F. WIRNITZER (Atti X Congr. Internaz. Chim., 1938, III, 46—57).—2-Chloro-4'-hydroxyazobenzene-3'-carboxylic acid gives (cf. A., 1936, 65) a Cr lake, $C_{39}H_{21}O_9N_6Cl_3Cr_2 \cdot 3H_2O$, which is an exception to the composition rule previously found, in that Cr : dye : $H_2O = 2 : 3 : 3$. The complex contains < the theoretical Cl, which has apparently been partly replaced by OH. The lake, $C_{42}H_{33}O_{12}N_6Cr_3 \cdot 3H_2O$, from 4-hydroxy-2'-methoxyazobenzene-3-carboxylic acid has Cr : dye : $H_2O = 1 : 3 : 3$, and differs from compounds previously described (e.g., in its solubility in org. solvents); it is regarded as a Cr^{III} salt, but contains < the theoretical OMe (apparently also partly replaced). The compound, $C_{51}H_{30}O_{18}N_6S_3Cr_2$, from 2-4'-hydroxy-3'-carboxybenzenazonaphthalene-6-sulphonic acid contains Cr : dye = 2 : 3; one Cr atom is regarded as linked ionically through $(-CO_2)_3$, the other in part through hydroxylic O, and in part co-ordinately through CO. With the azo-dye from $(p-NH_2 \cdot C_6H_4)_2S$ and salicylic acid (2 mols.), a Cr^{III} salt, $C_{78}H_{48}O_{18}N_6S_3Cr_2 \cdot 4H_2O$, in which Cr : dye : $H_2O = 2 : 3 : 4$, is obtained. Azosalicylic acid gives a compound, $C_{14}H_7O_6N_2Cr_2 \cdot 2H_2O$, in which the ratio is 1 : 1 : 2; with liquid NH_3 this gives a compound $+ 2H_2O, 2NH_3$; 5 : 2 : 1-NPh : $N \cdot C_6H_3(OH) \cdot CO_2H$ gives a Co lake, $C_{26}H_{17}O_6N_4Co \cdot 2H_2O$, of normal (1 : 2 : 2) metal : dye : H_2O ratio. 4 : 4'-Dihydroxystilbene-3 : 3'-dicarboxylic acid gives a Cr product of uncertain composition. The lakes are decomposed by boiling $AcOH-NaOAc$. E. W. W.

Optical activation of acids and a new resolution process depending on it. M. M. JAMISON and E. E. TURNER (J.C.S., 1940, 264—276; cf. A., 1938, II, 490).—4 : 6 : 4'-Tribromo-N-benzoyldiphenylamine-2-carboxylic acid (I) and nor-d- ψ -ephedrine in $CHCl_3$ afford two addition curves (*loc. cit.*), the "initial curve" representing rotations taken as soon as possible after mixing, and the "final curve" showing rotations after mutarotation is complete. With (I) and cinchonidine, activation increases rapidly with increase in acid : base ratio. The use of acids of moderate optical stability, solutions of which can be made more quickly than those of (I), allows "initial curves" to be made. Phenylbenzimidino-2-carbomethoxy-6-methylphenyl ether, m.p. 93°, isomerises at 260° to the Me ester, m.p. 106—107°, of N-benzoyl-6-methyldiphenylamine-2-carboxylic acid, m.p. 195—196° (previous softening); with the acid and nor-d- ψ -ephedrine in $CHCl_3$ mutarotation occurs when acid : base ratio is 0.5 : 1 (rotation becomes less positive); at 1 : 1 the amount of change increases, at 1.25 : 1 it is small, and at 2 : 1 extensive mutarotation occurs in the opposite sense, the positive rotation of the solution increasing. A similar result is obtained with cinchonidine in $CHCl_3-EtOH$ (40 : 1), the most generally used solvent (A). The equilibrium base-d acid \rightleftharpoons base-l acid is apparently displaced in one direction at low acid : base ratios, and in the other direction at high ratios. N-o-Tolylbenzimidino-2'-carbomethoxy-6-methylphenyl ether, m.p. 96—97°, at 290° gives the Me ester, m.p. 145°, of N-benzoyl-

2 : 6'-dimethyldiphenylamine-2'-carboxylic acid, m.p. 184° (previous softening) (also +1EtOH), which, however, solvated readily; mutarotation occurred with all the acid : base ratios used. N-Phenylbenzimidino-4 : 6-dichloro-2-carbomethoxyphenyl ether, m.p. 112—113°, isomerises at 220° to the Me ester, m.p. 117—119°, of 4 : 6-dichloro-N-benzoyldiphenylamine-2-carboxylic acid (II), m.p. 216—217° (softens from 209°); with nor-d- ψ -ephedrine in $CHCl_3$, activation begins at small acid : base ratios and increases steadily with addition of acid. With cinchonidine at acid : base ratios, e.g., 1 : 1, dextromutarotation occurs, whilst at, e.g., 3 : 1, levomutarotation occurs. Subsequent evaporation of the equilibrated solution at low temp., dissolution of the residual glass in C_6H_5N at -20°, and addition of this to cold dil. HCl gives an active acid (d or l respectively). (II) is so optically stable as to allow determination of the rate of racemisation of the d- and l-acid in (A) at 15° (vals. are given). Velocity coeffs. for equilibration of (II) and cinchonidine in (A) at different acid : base ratios, are determined. o- $C_6H_4Cl-NHBz$ (prep.) gives (method : A., 1938, II, 59) o-chlorophenylbenzimidino-2'-carbomethoxy-6'-methylphenyl ether, m.p. 85—86°, converted at 260—270° into the Me ester, m.p. 168—169°, of 2-chloro-N-benzoyl-6'-methyldiphenylamine-2'-carboxylic acid (III), 2 forms, m.p. 197—198° (varies with rate of heating). With cinchonidine and (III), no mutarotation is detected at acid : base ratios 0.5 : 1 or 1 : 1; at higher ratios there is slight activation. With brucine, there is much mutarotation at 0.5 : 1, increasing at 1 : 1; at higher ratios it decreased but was of the same sign, showing that the base-d acid is more stable than the base-l acid. Addition of Et_2O to equiv. amounts of brucine and (III) in $EtOH$ causes a second-order asymmetric transformation (*loc. cit.*), and almost all the salt crystallises as the brucine l-salt, $[\alpha]_D^{25} -383^\circ$ in (A), converted by HCO_2H-HCl into the partly racemised l-acid. With (III) and quinidine in (A) activation is greatest at ratio 1 : 1, but the speed of activation is increased with increased proportion of acid (mechanism discussed). Equilibration of (III)-quinidine mixtures is faster than the acid racemisation at the acid : base ratio of 1.5 : 1. The rate of racemisation of (III) in (A) in presence of 0.5 or 1 mol. of quinoline or 1 mol. of papaverine is \gg that for free acid; vals. are given. Theoretical aspects are discussed. N-Benzenesulphonyl-8-nitro-1-naphthylglycine (Mills *et al.*, A., 1928, 748) and brucine in warm MeOH give the brucine dl-salt. The brucine l-salt in C_6H_5N at -20°, added to dil. HCl, gives the l-acid. The addition curve for the dl-acid and brucine in $CHCl_3$ shows that the mutarotational effects are small. Mutarotation of a 1 : 1 mixture of acid : cinchonidine in pure $CHCl_3$ is pronounced; the equilibrium composition is cinchonidine d-, 38%, and l-salt, 62%; mutarotation is less in (A). Extraction of the respective equilibrated mixtures with dil. HCl gives solutions which from 1 : 1 and 2 : 1 acid : base mixtures are l-, and from 4 : 1, d-rotatory, and from 3 : 1, inactive. Activation in $EtOH$ is \ll in (A). A. T. P.

Action of bromine on vanillin, isovanillin, and their derivatives; modification of the directive

influence of hydroxyl in these compounds. L. C. RAIFORD and M. F. RAVELY (J. Org. Chem., 1940, 5, 204—211).—Bromination of vanillin (I), vanillic acid (II) and its Me ester (III), b.p. 140—141°/4 mm., m.p. 63—64° [from (II) and MeOH-HCl], vanillonitrile, and 4-nitroguaiacol (OH = 1) gives the 5-Br-derivative in each case; the *O*-acetates of (I)—(III) (no reaction with those of last two) afford 6-Br-derivatives. Bromination (method: Henry *et al.*, A., 1930, 1602) of isovanillin (IV) gives 33% of 2-bromoisovanillin [O-acetate, m.p. 82—84°; oxime, m.p. 174—176°, converted by pure Ac₂O into the acetate, m.p. 108—109.5°, of 2-bromoisovanillonitrile (V), m.p. 171—172.5°; 2-bromoisovanillic acid has m.p. 216.5—218°] and 55% of 6-bromoisovanillin [O-acetate, m.p. 106—107°; oxime, m.p. 224—226°, whence 6-bromoisovanillonitrile (VI), m.p. 162—163.5° (acetate, m.p. 165—167°)]. 5-Bromoisovanillin could not be prepared. *O*-Acetyl isovanillin (VII), m.p. 88—89° (lit. 64° and 88°) [from (IV) (in aq. KOH) and Et₂O-Ac₂O at ~0°], gives (method: Pschorr *et al.*, A., 1903, i, 175) the 5-NO₂-derivative, m.p. 119—120.5° (*loc. cit.*, 113°), reduced [Fe(OH)₂, aq. NH₃] to the NH₂-compound (not isolable in pure form). The oxime, m.p. 143—144°, of (IV) with Ac₂O affords isovanillonitrile, m.p. 130—132° (lit. 124°) (as acetate, m.p. 116—117°), brominated to (V) (32%) and (VI) (15%). Bromination of isovanillic acid gives 13% of the 6-Br-derivative (+0.5H₂O), m.p. 166.5—168.5°. Attempts to brominate (VII) were unsuccessful; with Br in AcOH-NaOAc-I (catalyst) at 100° (bath) *O*-acetyl isovanillic acid (VIII), m.p. 216—218° (lit. 206—207°), is formed. Br (50% excess) and (VIII) in AcOH-NaOAc at 100° (bath)/8—10 hr. afford ~12% of 2:5:1-OMe-C₆H₃Br-OAc by replacement of CO₂H with Br. 3-Acetoxy-4-methoxybenzylidene diacetate, m.p. 118—119° [from (IV) and Ac₂O-conc. H₂SO₄], does not react with Br. *Me* 5-bromovanillate, m.p. 152—152.5°, is obtained from (III) and Br (slightly >1 equiv.) in AcOH-NaOAc-I; *Me* *O*-acetylvanillate, m.p. 75.5—76° [from (III) and Ac₂O-H₂SO₄], similarly gives 30% of its 6-Br-derivative, m.p. 95—95.5°, hydrolysed (KOH) to 6-bromovanillic acid, m.p. 190—191°. The above results show that acylation of OH suppresses its directive influence and that OAlk tends to direct more strongly to *p* than *o*.

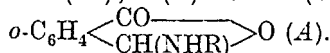
H. B.

5-Nitro- α -*p*-dimethylaminobenzylidene- and 5-amino- α -*p*-dimethylaminobenzyl-phthalide. R. L. SHRINER and L. S. KEYSER (J. Org. Chem., 1940, 5, 200—203).—5-Nitrophthalide (I), m.p. 145° (Borsche *et al.*, A., 1934, 652), does not undergo the Mannich reaction (with CH₂O and NHET₂). *p*-NMe₂-C₆H₄-CHO, (I), and a little piperidine at 185—190°/1 hr. give 85% of 5-nitro- α -*p*-dimethylaminobenzylidenephthalide (II), 3 polymorphic forms, m.p. (Köfler) 283—284°, which is pptd. from its solution in 10% HCl by H₂O and dyes wool a bright rust colour (fast to washing and ultra-violet light). Reduction (H₂ at ~2000 lb., Raney Ni, dioxan, 90° or H₂, PtO₂, 50% H₂SO₄, 3 atm.) of (II) affords 5-amino- α -*p*-dimethylaminobenzylidenephthalide, m.p. 259—262° (*Ac* derivative, m.p. 287°), and then (fresh catalysts) 5-amino- α -*p*-dimethylaminobenzylphthalide, m.p. 204.5° (*Ac* derivative, m.p. 210°).

H. B.

(A) Action of succinic and phthalic anhydrides, and of *o*-phthalaldehydic acid on Schiff's bases. A. LUDWIG and R. I. GEORGESCU. (B) Action of benzoic, propionic, and hexoic anhydrides on the azomethine bridge. A. LUDWIG and S. TACHE. (C) Azomethine bridge. R. I. GEORGESCU (Bul. Chim. Soc. Române, 1938, 39, 41—63, 87—100, 115—126).—(A) (CH₂CO)₂O (I) reacts with Schiff's bases (in anhyd. solvents such as PhMe or CHCl₃, or in the fused state) as follows: (I) + CHPh:NR → NHR·CO·[CH₂]₂·CO₂H + PhCHO [R = Ph, *o*-, *m*-, and *p*-C₆H₄·CO₂H, and 1:2:4-C₆H₃(OH)·CO₂Me]. N-2-Hydroxy-4-carbomethoxyphenylsuccinamic acid and 2-hydroxy-4'-carbomethoxybenzylideneaniline (II) have m.p. 181—182° and 92—93°, respectively. (I) and *p*-NH₂·C₆H₄·CO₂Et afford N-*p*-carbomethoxyphenylsuccinamic acid, m.p. 161°. *o*-C₆H₄(CO)₂O (III) reacts similarly to (I) in solution, yielding substances of the general formula *o*-CO₂H·C₆H₄·CO·NHR [R = Ph, *o*-, *m*-, and *p*-C₆H₄·CO₂H, 1:2:4-C₆H₃(OH)·CO₂Me, *p*-C₆H₄·CO₂Et]; in absence of a solvent, the products are phthalimides,

$$o\text{-C}_6\text{H}_4\text{<}\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\text{>NR}$$
 [R = Ph, *o*-, *m*-, and *p*-C₆H₄·CO₂H, 1:2:4-C₆H₃(OH)·CO₂Me]. N-*p*-Carbomethoxy- and N-2-hydroxy-4-carbomethoxy-phenylphthalamic acids have m.p. 174—175° and 229°, respectively; N-2-hydroxy-4-carbomethoxyphenylphthalimide has m.p. 229°. The products obtained with piperonylidene-*p*-toluidine are piperonal and N-*p*-tolylphthalimide. *o*-CH₂O·C₆H₄·CO₂H (IV) fused with CHPh:NPh, *m*-CO₂H·C₆H₄·N:CHPh, and (II) gives the anil, *m*-carboxyanil (V), m.p. 241—242°, and 2-hydroxy-4-carbomethoxyanil (VI), m.p. 240—241°, respectively, of (IV); (V) and (VI) are formulated as



(B) Acid anhydrides react with substituted benzylideneanilines as follows: CHPh:NR + (R'CO)₂O → CHPh(O·COR')·NR·COR' (+H₂O) → NHPh·COR' + R'CO₂H + PhCHO (R' = Ph, R = Ph, *o*-, *m*-, and *p*-C₆H₄·CO₂H, α -C₁₀H₇, *p*-C₆H₄·OEt, *p*-C₆H₄·NO₂; R = Et or *n*-C₅H₁₁, R = Ph, *p*-C₆H₄·NO₂, *p*-C₆H₄·OEt).

(C) The reactions (above) with (I), (III), and (IV) are extended to R = *p*-NO₂·C₆H₄ and *p*-OEt·C₆H₄. The *p*-nitroanil, m.p. 243°, and *p*-ethoxyanil, m.p. 175°, of (IV) are formulated as (A). R. T.

Synthesis of phenanthrene derivatives. I. Phenanthrene-9:10-dicarboxylic anhydride and -9-carboxylic acid. T. A. GEISSMAN and R. W. TESS (J. Amer. Chem. Soc., 1940, 62, 514—516; cf. Schönberg *et al.*, A., 1940, II, 45).—*o*-C₆H₄Ph·CH₂·CN (prep. starting from *o*-C₆H₄Ph·CN described; cf. von Braun *et al.*, A., 1929, 561) and H₂SO₄-EtOH give Et *o*-diphenylacetate, b.p. 180—185°/15 mm., which with Et₂C₂O₄ and KOEt in Et₂O-EtOH gives *o*-C₆H₄Ph·CH(CO₂Et)·CO·CO₂Et, an oil, converted by 48% HBr into phenanthrene-9-carboxylic acid (67%) and -9:10-dicarboxylic anhydride (13%), m.p. 310—315° (lit. 312°, 322°). R. S. C.

Sterols. XCIV. Persulphate oxidation of allopregnane derivatives. R. E. MARKER, E. ROHRMANN, E. L. WITTE, H. M. CROOKS, jun., and

E. M. JONES (J. Amer. Chem. Soc., 1940, **62**, 650—651).—*allo*Pregnan-20-one, $K_2S_2O_8$, and H_2SO_4 in boiling 90% AcOH give α ioallocholanolic acid, m.p. 228—230° (Me ester, m.p. 141—143°; cf. Tschesche, A., 1935, 342), and inseparable mixed *carbinols*, $C_{19}H_{32}O$, m.p. 110—142°. *allo*Pregnan-3(β)-ol-20-one gives similarly 3(β)-hydroxy α ioallocholanolic acid and mixed *carbinols*, converted by CrO_3 into androstenedione. R. S. C.

Sterols. XCI. Oxidation of 3:6-diacetoxycholestane. R. E. MARKER, J. KRUEGER, J. R. ADAMS, jun., and E. M. JONES (J. Amer. Chem. Soc., 1940, **62**, 645—646).—Cholestane-3:6-diol (A., 1940, II, 96), m.p. 191°, is prepared by hydrogenation (PtO_2) of 6-hydroxycholestanone in 95% EtOH at 3 atm. or of 6-ketocholestanol in AcOH. Its diacetate and CrO_3 in AcOH at 90° give *allo*hydroxycholelic acid, m.p. 280° [Me ester (I), m.p. 179° (lit. 181°)], and 6-hydroxyisoandrosterone (II), m.p. 205°, isolated as *diacetate semicarbazone*, m.p. 222°, which gives (II) by hydrolysis first with boiling H_2SO_4 -EtOH- H_2O and then with 2% KOH-MeOH. Bisnorhydroxycholelic acid and CrO_3 -AcOH at 12—15° give 3:6-diketobisnorcholanic acid, m.p. 185° (Me ester, m.p. 170°), which with boiling HCl-AcOH gives 3:6-diketobisnorallocholanolic acid, m.p. 244° (Me ester, m.p. 211°), hydrogenated (PtO_2 ; AcOH; 3 atm.) to *bisnorallohydroxycholelic acid*, m.p. 259° [Me ester, m.p. 233°; *diacetate* (+0.5MeOH), m.p. 115° (Me ester, m.p. 135°)]. Me *allo*hydroxycholelate with $MgPhBr$, followed by acetylation, dehydration, and oxidation (CrO_3), gives *norallohydroxycholelic acid*, m.p. 225°. R. S. C.

Preparation and degradation of lithocholic acid. W. M. HOEHN and H. L. MASON (J. Amer. Chem. Soc., 1940, **62**, 569—570).—Me deoxycholelate, $BzCl$, and C_6H_5N in C_6H_6 at 5° give *Me 12-hydroxy-3-benzoyloxycholelate*, +0.5Et $_2O$, m.p. 78—80° (gas) (or with 2 mols. of $BzCl$ the dibenzoate, m.p. 145—146°), oxidised by CrO_3 -AcOH at 15° (later 0°) to Me 12-keto-3-benzoyloxycholelate, m.p. 94—95°, the *semicarbazone*, m.p. 160—162°, of which with $NaOEt$ -EtOH at ~200° gives lithocholic acid, m.p. 183—185°, $[\alpha]_D^{25} + 34^\circ$, $[\alpha]_D^{25} + 39^\circ$, also obtained from Me 7:12-diketo-3-benzoyloxycholelate *disemicarbazone* by $NaOMe$ -MeOH at $174 \pm 5^\circ$. α Etiolithocholic acid, m.p. 270—272°, and CrO_3 -AcOH at 15° give dehydro α etiolithocholic acid (4-*Br*-derivative, m.p. 190—192°). $\alpha\alpha$ -Diphenyl- β -3-acetoxybisnorcholanyl-, m.p. 158—160°, $[\alpha]_D^{25} + 75.5^\circ$ in $CHCl_3$, and - β -3-acetoxypregnanyl-ethylene, m.p. 150—152°, $[\alpha]_D^{25} + 140 \pm 3^\circ$ in $CHCl_3$, ? $\alpha\alpha$ -diphenyl- β -3-acetoxy α iocholanyl- Δ^a -propene, m.p. 158—160°, $[\alpha]_D^{25} + 398 \pm 2^\circ$ in $CHCl_3$, *pregnan*-3(α)-ol-20-one, m.p. 148—149°, $[\alpha]_D^{25} + 129 \pm 3^\circ$ in EtOH (21-*CHPh*: derivative, m.p. 228—230°, $[\alpha]_D^{25} + 181 \pm 3^\circ$ in EtOH), and 3-acetoxy α iocholanic acid, m.p. 226—229°, $[\alpha]_D^{25} + 86.4 \pm 3^\circ$ in EtOH, are described. The following corrections in nomenclature are recorded (cf. A., 1938, II, 329): *diphenyl*-3:12-diacetoxymisnor- for *diphenyl*-3:12-diacetoxynorcholanyl-ethylene; *diphenyl*-3:12-diacetoxypregnanyl- for *diphenyl*-3:12-diacetoxymisnorcholanyl-ethylene; ? $\alpha\alpha$ -

diphenyl- β -3:12-diacetoxy α iocholanyl- Δ^a -propene for *diphenyl*-3:12-diacetoxymisnorcholanyl-ethylene.

R. S. C.

Carboxylic acids of the cyclopentanopolymethylenanthrene series.—See B., 1940, 324.

Synthesis of vitamin-A. P. KARRER and A. RÜEGGER (Helv. Chim. Acta, 1940, **23**, 284—287).—A series (A) of different polyenes results from the condensation of β -ionylideneacetaldehyde and β -methylcrotonaldehyde in presence of piperidine. The main product gives a blue colour with $SbCl_3$ but appears to differ spectrographically and chromatographically from vitamin-A (I); it is, however, too impure to be diagnosed. The possibility that (I) is present with other polyenes in (A) is not excluded.

H. W.

Aromatic acetals. R. JUSTONI (Atti X Congr. Internaz. Chim., 1938, III, 226—229).— $PhCHO$ (I) and $CH_2Ph \cdot OH$ (II) are boiled together until H_2O no longer distils, and unchanged (I) and (II) are removed by distillation at 15—20 mm.; the syrupy residue consists of $PhCHO$ dibenzyl acetal (III), m.p. 30—31°, purified through dissolution in EtOH and addition of H_2O . $PhCHO$ di- β -phenylethyl acetal, m.p. 28—29°, is prepared similarly. $CHPh \cdot CH \cdot CHO$ dibenzyl and di- β -phenylethyl acetal are not obtained crystalline. The acetals are stable at 90—100°, but on keeping in air slowly decompose. They are readily hydrolysed by dil. acids, or by Ac_2O or $BzCl$. When heated, (III) gives (I) and $PhMe$.

E. W. W.

$\alpha\beta$ -Unsaturated aldehydes of the pregnene series. H. REICH (Helv. Chim. Acta, 1940, **23**, 219—224).—21-Bromo-3-acetoxy- $\Delta^{5:17}$ -pregnadiene and anhyd. C_5H_5N at room temp. give the *pyridinium bromide*, m.p. 216—217° (corr.), which is converted by $p-NO \cdot C_6H_4 \cdot NMe_2$ and $NaOH$ into the corresponding *nitron*, m.p. ~170° (with probably the OH-compound, m.p. 133—135°). This is transformed by 2*N*-HCl into 3-acetoxy- $\Delta^{5:17}$ -pregnadien-21-al, m.p. 183—186°. Similarly, 21-bromo- $\Delta^{4:17}$ -pregnadien-3-one yields successively the *pyridinium bromide* (I), m.p. 213—214° (corr.; decomp.), the *nitron*, m.p. 152—155° (corr.) after softening at 148°, and 3-keto- $\Delta^{4:17}$ -pregnadien-21-al, m.p. 147—152° (corr.). Thermal decomp. of (I) appears to yield somewhat impure $\Delta^{4:16:20}$ -pregnatrien-3-one.

H. W.

Ionones and hydrones. A. GIACALONE (Atti X Congr. Internaz. Chim., 1938, **3**, 186—189; cf. A., 1937, II, 502).— β -Ionone (I) and MeI in boiling EtOH- $NaOEt$ give *methyl- β -ionone*, b.p. 111—115°/4.5 mm. [*p*-bromo-, m.p. 129—130° (softens 123°), and 2:4-dinitro-phenylhydrazones, m.p. 114—115° (sinters 110°)]. (I) and EtI in EtOH- $NaOEt$ give *ethyl- β -ionone*, b.p. 121—123°/6.5 mm. [*p*-bromo-, m.p. 123°, and 2:4-dinitro-phenylhydrazones, m.p. 127—128° (sinters 125°)].

E. W. W.

Reaction of aliphatic esters with benzene in presence of aluminium chloride. D. N. KURSANOV and R. R. ZELVIN (J. Gen. Chem. Russ., 1939, **9**, 2173—2178).— $EtOAc$ in C_6H_6 and $AlCl_3$, at the b.p., yield $PhEt$ and $p-C_6H_4Et \cdot COMe$. Pr^aOAc similarly yields $PhPr^a$, $PhPr^b$, and *p*-*n*-propylphenyl *Me ketone*, b.p. 75—80°/70 mm. (*semicarbazone*, m.p.

187.3—188.5°); Bu^oOAc gives PhBu^o and *p*-*n*-butylphenyl Me ketone, b.p. 148—152°/19 mm. (semicarbazone, m.p. 189.5—190.5°); HCO₂Et affords PhEt, C₆H₄Et₂, and C₆H₃Et₃. EtOAc and AlCl₃ yield a complex compound, which decomposes at 70° in presence of AlCl₃. The reaction is represented: $R\cdot CO_2R' + AlCl_3 \rightarrow R\cdot CO_2AlCl_2 + R'Cl$; $R'Cl + C_6H_6 \rightarrow PhR' + HCl$; $R\cdot CO_2AlCl_2 + PhR' \rightarrow COR\cdot C_6H_4R' + AlOCl + HCl$. R. T.

Action of heat on bromonitro-compounds. C. F. H. ALLEN and C. V. WILSON (J. Org. Chem., 1940, 5, 146—156).—Equiv. amounts of CHPh:CH·COAr and CH₂Ph·NO₂ in (usually) MeOH—NaOMe followed by MeOH—AcOH give *p*-chlorophenyl, stereoisomeric forms, m.p. 171° and 116°, *p*-bromophenyl, forms, m.p. 180° and 125°, *p*-diphenyl, m.p. 180°, and 2-methyl-5-isopropylphenyl, m.p. 147°, γ -nitro- β -diphenylpropyl ketone. These with Br in MeOH—NaOMe (slightly >1 equiv.) afford the γ -Br-derivatives; *p*-chlorophenyl, m.p. 126°, *p*-bromophenyl, m.p. 157°, and 2-methyl-5-isopropylphenyl, m.p. 138°, γ -bromo- γ -nitro- β -diphenylpropyl ketones are new. Pyrolysis of NO₂·CPhBr·CHPh·CH₂·COAr (either form) at 180—200°/15—20 min. gives N oxides and 4-bromo-2:3-diphenyl-5-arylfuran, probably by way of CPh·CHPh·CH₂·COAr which is then brominated at C_{4a} and so yields the furan (cf. A., 1930, 217). 4-Bromo-2:3:5-triphenyl, m.p. 129°, -2:3-diphenyl-5-*p*-bromophenyl, m.p. 157°, and -2:3-diphenyl-5-*p*-diphenylfuran, m.p. 193°, are new. Pyrolysis of NO₂·CHPh·CHPh·CH₂·COPh affords CHPh:CH·COPh and N oxides + PhCHO (from CH₂Ph·NO₂). CHPh:CHBr·NO₂ at 190—200° gives (mainly) CPhBr:CHBr (I), a little BzOH, and a considerable C residue; it is considered that the intermediate radical CHPh:C< rearranges to CPh:CH which then adds Br to form (I). β -Bromo- β -nitro- α -diphenylethylene, m.p. 91° (from CPh₂:CH·NO₂ and Br in CHCl₃), heated to 300° (bath) affords CPh₂:CBr₂; transitory existence of the radical CPh₂:C< is postulated. *p*-C₆H₄Ph·CPh:CH₂ and dry nitrous fumes in CCl₄ at <0° give β -nitro- α -phenyl- α -*p*-diphenylethyl alcohol, m.p. 136°, and gummy material, which is dehydrated (AcCl) to β -nitro- α -phenyl- α -*p*-diphenylethylene, forms m.p. 134° and 114°, oxidised (KMnO₄, COMe₂) to *p*-C₆H₄Ph·COPh. CHMeBr·NO₂ undergoes some decomp. during distillation. Other examples (lit.) of thermal decomp. of compounds containing >CBr·NO₂ are discussed. H. B.

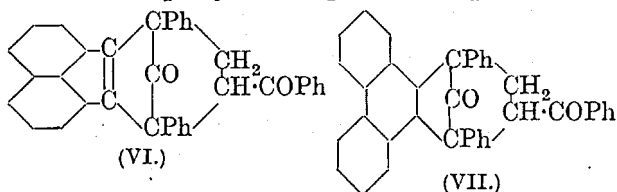
Relation between chain-length and orientation in acylation of phenol. A. W. RALSTON and S. T. BAUER (J. Org. Chem., 1940, 5, 165—170).—The ratio of *o*- (I) to *p*-OH·C₆H₄·COR (II) obtained from PhOH, RCOCl (R = C₇H₁₅, C₁₁H₂₃, C₁₃H₂₇, C₁₅H₃₁, and C₁₇H₃₅), and AlCl₃ in C₂H₂Cl₄ at ~55—60° decreases with increase in size of R. The yields of (I) are 50, 32.6, 31.9, 25.4, and 27.8, and those of (II) are 12, 24.6, 36.7, 28.5, and 28%, respectively; (I) and (II) are separated by the method of Baltzly *et al.* (A., 1933, 1287). The following are described: *o*-hydroxyphenyl heptyl, b.p. 97—99°/1 mm. (140—141°), undecyl, m.p. 44—45.5° (92—93°), tridecyl, m.p. 52—55° (92—92.5°), pentadecyl, m.p. 54—56°

(94—95°), and heptadecyl ketone, m.p. 64—66° (96—97°); *p*-hydroxyphenyl heptyl, m.p. 62.5—63.5° (176—178°), undecyl, m.p. 71—72° (150—151°), tridecyl, m.p. 78—80° (142—143°), pentadecyl, m.p. 84.5—85° (141—142°), and heptadecyl ketone, m.p. 87—89° (139.5—140°); temp. in parentheses are the m.p. of the 2:4-dinitrophenylhydrazones. (II) are identified by oxidation (HNO₃) of their Me ethers to anisic acid. H. B.

Constitution and synthesis of conglomerone. F. N. LAHEY and T. G. H. JONES (Univ. Queensland Paper, 1939, 1, No. 12, 4 pp.).—Conglomerone [2:4:6-trimethoxyisobutyrophenone] (I), isolated from *E. conglomerata* oil (Proc. Roy. Soc. Queensland, 1938, 10) had m.p. 62—62.5° (2:4-dinitrophenylhydrazone, m.p. 164°). With Beckmann's CrO₃ mixture (I) gave 2:6-dimethoxy-*p*-benzoquinone, and with NaOH—EtOH at 160° (I) gave Pr^oCO₂H, an unidentified neutral product, and a phenol giving, with Me₂SO₄, 1:3:5-C₆H₃(OMe)₃. Pr^oCOCl, 1:3:5-C₆H₃(OMe)₃, and FeCl₃ in CS₂ give (I). T. F. W.

Addition reactions of phenyl vinyl ketone. VI. Diene synthesis. C. F. H. ALLEN, A. C. BELL, A. BELL, and J. VAN ALLAN (J. Amer. Chem. Soc., 1940, 62, 656—664; cf. A., 1935, 1124).—(CPh:CH)₂ and CPh:CH:CH₂ (I) {prep. *in situ* from CPh:[CH₂]₂·Cl (or, less well, CPh:[CH₂]₂·NAlk₂·HCl) and NaOAc} in boiling xylene give (60 hr.) 4-benzoyl-1:2-diphenyl- Δ^1 -cyclohexene, m.p. 83° (2:4-dinitrophenylhydrazone, m.p. 203°), dehydrogenated by Br·CHCl₃ to 3:4:1-C₆H₃Ph₂·COPh (cf. A., 1933, 1164) (2:4-dinitrophenylhydrazone, m.p. 248°), which with NaNH₂ in cymene gives *o*-C₆H₄Ph₂ and 3:4:1-C₆H₃Ph₂·CO₂H. (CHPh:CH)₂ adds (I) less readily to give a syrup, b.p. 250—255°/4—5 mm., which with S at 200° gives 2:5-diphenylbenzophenone, m.p. 130°, converted by NaNH₂ into *p*-C₆H₄Ph₂. (CMe:CH)₂ and (I) give 4-benzoyl-1:2-dimethyl- Δ^1 -cyclohexene, b.p. 163—165°/6 mm. (2:4-dinitrophenylhydrazone, m.p. 152°; dibromide, m.p. 132°), dehydrogenated by S at 190—230° to 3:4:1-C₆H₃Me₂·COPh (2:4-dinitrophenylhydrazone, m.p. 252°). CHPh:CH·CH:CHMe and (I) give 4- or 5-benzoyl-3-phenyl-6-methyl- Δ^1 -cyclohexene, m.p. 61°, b.p. 157—159°/1 mm. (dibromide, m.p. 125°). cyclopentadiene gives 3-benzoyl-1:4-endomethylene- Δ^5 -cyclohexene, b.p. 122—124°/3 mm. (semicarbazone, m.p. 178—180°). Isoprene and (I) in PhMe at 100° give a product containing 4-benzoyl-1-methyl- Δ^1 -cyclohexene, b.p. 120—122°/2 mm. (2:4-dinitrophenylhydrazone, m.p. 137°). Phellandrene in EtOH gives a mixture, and cyclohexadiene gives only (in EtOH) CPh:[CH₂]₂·OEt. 10-Methylene-9-anthrone (II) and (I) in PhNO₂ at 180—190° give 3-benzoyl-benzanthrone (III), m.p. 192°, also obtained from benzanthrone-3-carboxyl chloride, C₆H₆, and AlCl₃ at 70°. CrO₃—AcOH—H₂O, first at room temp. and then boiling, oxidises (III) to *Ph 1-anthraquinonyl diketone* (IV), m.p. 174°, converted by Na₂O₂—H₂O at 70° into anthraquinone-1-carboxylic acid. AlCl₃—NaCl and (III) at 180—200° give 4:5:9:10-dibenzpyrene-3:8-quinone. Tetraphenylcyclopentadienone and (I) in boiling PhMe or, less well, alone at 130° give 1:4-endoketo-3-benzoyl-1:4:5:6-tetra-

phenyl- Δ^5 -cyclohexene, m.p. 210° (decomp.), converted by pyrolysis (215°) into 2:3:4:5-tetraphenyl-2:5- or -1:6-dihydrobenzophenone (V), forms, m.p. 177° and 158—159° (latter obtained by carrying out the addition in boiling $C_6H_5Cl_3$; former in $PhNO_2$ or by pyrolysis). Br, $KMnO_4$ - $COMe_2$, or S (240—250°) and (V) give 2:3:4:5-tetraphenylbenzophenone, m.p. 190°, converted by $NaNH_2$ in *p*-cymene into 1:2:3:4- $C_6H_5Ph_4$. 2:5-Diphenyl-3:4-1':8'-naphthylenecyclopentadienone and (I) in $PhMe$ give the substance (VI), m.p. 189—190°, which readily, e.g., in hot $AcOH$, loses CO to give 2:5-diphenyl-3:4-1':8'-naphthylenebenzophenone, m.p. 194—195°.



2:5-Diphenyl-3:4-*oo'*-diphenylenecyclopentadienone with (I) gives the substance (VII), m.p. 273°, but with $COPh \cdot CH \cdot CH \cdot NMe_2$ gives a product, $C_{36}H_{24}O_2$, m.p. 312—315°. $(CPh \cdot CH_2)_2$ and $COPh \cdot CH \cdot CH \cdot CO_2Me$ at 165° (52%) or in boiling xylene (20% yield) give *Me* 2-benzoyl-4:5-diphenyl- Δ^4 -tetrahydrobenzoate, m.p. 147° [Br_2 -derivative, m.p. 183° (decomp.), formed in warm $CHCl_3$], converted by S at 230°, followed by hot KOH - $EtOH$, into 4:5:2:1- $C_6H_5Ph_2Bz \cdot CO_2H$. Et sorbate and (I) give mixed esters (A), hydrolysed to stereoisomeric 2-benzoyl-4-methyl- Δ^5 -tetrahydrobenzoic acids, of which one form, m.p. 162—163°, is obtained pure. Dehydrogenation, hydrolysis, and ring-closure (20% oleum) converts (A) into 2-methyl-anthraquinone. Tetraphenylenecyclopentadienone and $COPh \cdot CH \cdot CHPh$ in boiling $C_6H_5Cl_3$ give (cf. A., 1934, 1102) $C_6Ph_5 \cdot COPh$, m.p. 338° (uncorr.), 341° (corr.), whence $NaNH_2$ yields C_6HPh_5 . *trans*-($CH \cdot COPh$)₂ and (II) in $C_6H_5Cl_3$ and $PhNO_2$ give 2:3-dibenzoyl-benzanthrone, dimorphic, m.p. 286° and 208°, oxidised by CrO_3 to (IV). Mono- and di-meric (I) are isolated. Furan, sylvan, and 2:5-dimethyl-furan do not add (I).

R. S. C.

Preparation of optically active semicarbazides, and a resolution of benzoin. A. J. LITTLE, J. M'LEAN, and F. J. WILSON (J.C.S., 1940, 336—338; cf. A., 1928, 1247).—*r*- α -Phenylpropylamine (I) and *l*-malic acid in $EtOH$ give the *d*-amine *l*-*H* malate, m.p. 169°, $[\alpha]_D^{25} -11.68^\circ$ in H_2O , and thence by 50% aq. KOH , *d*- α -phenylpropylamine (II), b.p. 204—206°, $[\alpha]_D^{25} +20.15^\circ$ (cf. Billon, A., 1927, 879); the *l*-amine (III), $[\alpha]_D^{25} -19.85^\circ$, is purified through the *d*-*H* tartrate, m.p. 179°, $[\alpha]_D^{25} +22.65^\circ$ in H_2O . (I), (II), or (III) and $COMe_2 \cdot N \cdot NH \cdot CO \cdot NH_2$ in xylene give *acetone-r*-, m.p. 110°, -*d*-, m.p. 92°, and -*l*- δ -(α -phenylpropyl)semicarbazone, m.p. 92°, and thence by $N \cdot HCl$, *r*-, m.p. 135°, *d*- (IV), m.p. 165°, $[\alpha]_D^{25} +67.5^\circ$ in H_2O , and *l*- δ -(α -phenylpropyl)semicarbazide hydrochloride (V), m.p. 165°, $[\alpha]_D^{25} -67.3^\circ$ in H_2O , respectively. *r*-Benzoin and (IV) in C_5H_5N at room temp. (1 week) give *d*-benzoin-*d*- δ -(α -phenylpropyl)-semicarbazone (VI), m.p. 166°, $[\alpha]_D^{25} -126.0^\circ$ in $EtOH$, hydrolysed by aq. $EtOH-H_2SO_4$ at 100° (bath) to *d*-benzoin, m.p. 133—134°, $[\alpha]_D^{25} +118.1^\circ$ L (A., II.)

in $COMe_2$. Hydrolysis of the mother-liquor from (VI) gives *l*-benzoin, m.p. 133—134°, $[\alpha]_D^{25} -116.6^\circ$ in $COMe_2$, almost optically pure. *r*-Benzoin and (V) in C_5H_5N give *l*-benzoin-*l*- δ -(α -phenylpropyl)semicarbazone, m.p. 166°, $[\alpha]_D^{25} +127.1^\circ$ in $EtOH$, and thence pure *l*-benzoin. In unsuccessful attempts to resolve *r*-camphor, the following are prepared: *r*-camphor-*r*-, m.p. 137°, and -*l*- (VII), m.p. 104°, $[\alpha]_D^{25} +61.1^\circ$ in $EtOH$, *d*-camphor-*d*-, m.p. 118°, $[\alpha]_D^{25} -93.6^\circ$ in $EtOH$, and *l*-camphor-*d*- δ -(α -phenylpropyl)semicarbazone, m.p. 120°, $[\alpha]_D^{25} -38.8^\circ$ in $EtOH$ [equal amounts of the last two compounds from aq. $EtOH$ give a compound, m.p. 104°, resembling (VII), but having $[\alpha]_D^{25} -61.6^\circ$ in $EtOH$]; *r*-camphor-*r*-, m.p. 144° (from *r*-camphorsemicarbazone and *r*- α -phenylethylamine at 180°), *d*-camphor-*l*- (VIII), m.p. 112°, $[\alpha]_D^{25} +41.3^\circ$ in $EtOH$, *l*-camphor-*l*- (IX), m.p. 112°, $[\alpha]_D^{25} +102.4^\circ$ in $EtOH$, and *r*-camphor-*l*- δ -(α -phenylethyl)semicarbazone, m.p. 122—123°, $[\alpha]_D^{25} +68.9^\circ$ in $EtOH$ [also from (VIII) + (IX) in $EtOH$]. *r*-2-Imino-5-methylthiazolidine and *d*-camphor-10-sulphonic acid in $EtOH$ give the *d*-camphor-sulphonate (X), m.p. 182—184°, $[\alpha]_D^{25} -19.63^\circ$ in H_2O , of the *l*-base, and thence by aq. KOH and dil. HCl , 1-2-imino-5-methylthiazolidine hydrochloride, m.p. 175°, $[\alpha]_D^{25} -76.5^\circ$ in H_2O . The crude *d*-base, from the mother-liquors from (X), and *l*-camphor-10-sulphonic acid in $EtOH$ give the *d*-base *l*-camphor-sulphonate, m.p. 182—184°, $[\alpha]_D^{25} +20.1^\circ$ in H_2O , and thence *d*-2-imino-5-methylthiazolidine hydrochloride, m.p. 172—173°, $[\alpha]_D^{25} +77.5^\circ$ in H_2O . 3-Methylcyclohexanone does not give a suitable product with δ -(α -phenylethyl)semicarbazide.

A. T. P.

Mechanism of the reaction between arylamines and benzoin. R. M. COWPER and T. S. STEVENS (J.C.S., 1940, 347—349).—*Ph* *p*-methoxybenzyl ketone (prep. given) and Br in Et_2O (+ a trace of $AlCl_3$) give the α -Br-derivative, converted by NH_2Ph at 100° (bath) into *Ph* α -anilino-*p*-methoxybenzyl ketone (I), m.p. 135—136°. Similarly prepared are *Ph* α -*p*-toluidino- (II), m.p. 119—120°, and α -methyl-anilino-*p*-methoxybenzyl ketone (III), m.p. 118—119°; *p*-anisyl α -anilino-, m.p. 144—145° (IV), α -*p*-toluidino-, m.p. 142—143°, and α -methyl-anilino-benzyl ketone, m.p. 160—161°. Benzanisoin (V), NH_2Ph or *p*- $C_6H_4Me \cdot NH_2$, and P_2O_5 at 100° (bath) give (I) ($NHAr$ attached to C of original CO) or (II), respectively, but $NHPhMe$ gives no reaction at <170°. Similarly *p*- $OMe \cdot C_6H_4 \cdot CHBz \cdot OH$ gives (IV). (V) and $SOCl_2$ give a syrup, converted by NH_2Ph into (IV). (I) and $Me_2SO_4 \cdot C_6H_5 \cdot Na_2CO_3$ give (III) (best method of prep.). (I) or (IV) and Zn dust in 20% H_2SO_4 at 100° (bath) give *Ph* *p*-methoxybenzyl or *p*-anisyl benzyl ketone, respectively. The initial point of attack by NH_2Ph on benzoin is the CO group and $NPh \cdot CPh \cdot CHPh \cdot OH$, first formed, spontaneously gives $NHPh \cdot ClPhBz$.

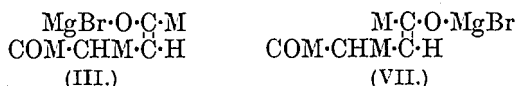
A. T. P.

Bis-*p*-carboxyphenylhydrazones, decomp. 318—320°, of *p*-tolylglyoxal, and compound, m.p. 172—175°, from *p*-tolacyl alcohol and *p*-carboxyphenylhydrazine.—See A., 1940, III, 346.

Keto-cyclol tautomerism of $\alpha\zeta$ -diketones. $\alpha\delta$ -Dibromo- $\alpha\delta$ -dibenzoylbutane [$\beta\epsilon$ -dibromo- $\alpha\zeta$ -di-

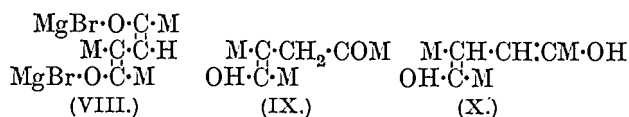
keto- $\alpha\zeta$ -diphenyl- n -hexane]. T. Y. KAO (J. Amer. Chem. Soc., 1940, **62**, 356—358).— $(\text{CH}_2\cdot\text{CHBr}\cdot\text{COPh})_2$ (I) reacts mainly as 2 : 5-dibromo-5-benzoyl-1-phenylcyclopentanol. Analogous reactions are reviewed. With "mol." Ag in boiling COMe_2 , (I) gives 37% of 1 : 2-epoxy-5-benzoyl-1-phenylcyclopentane (II) and 13% of *cis*-1 : 2-dibenzoylcyclobutane. With NH_4Et_2 in C_6H_6 , (I) gives 5-bromo-1 : 2-epoxy-5-benzoyl-1-phenylcyclopentane (III) (59%), obtained also in poor yield by NaCN or NaOAc and in 64% yield by $\text{CHNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 -EtOH. With Zn dust and NaI in boiling COMe_2 , (III) gives a poor yield of (II). R. S. C.

$\alpha\beta\delta$ -Trimesityl $\alpha\delta$ -diketones and related compounds, including the stereoisomeric mono- and di-enols. R. E. LUTZ and C. J. KIBLER (J. Amer. Chem. Soc., 1940, **62**, 360—372).— $\alpha\beta\delta$ -Trimesityl-*n*-butane- $\alpha\delta$ -dione (I) and various of its mono- and di-enolic forms are prepared. Structures assigned are based on the easier enolisation of $\text{CH}_2\cdot\text{COM}$ (here and below M = mesityl) compared with $\text{CHM}\cdot\text{COM}$, on the more ready ketonisation of $\text{CH}\cdot\text{CM}\cdot\text{OH}$, and on the relative ease of cyclisation. The results are consistent with the view that furan formation involves addition of an enolic OH to γ -CO followed by loss of a mol. of H_2O (cf. A., 1939, II, 429). Addition of $(\text{CH}\cdot\text{COM})_2$ (II) to MgMBr (4 equivs.) in Et_2O at 20° gives the Mg mono-enolate-A (III), which with dil. HCl gives the diketone (I), m.p. 147 — 147.5° (Br gives no cryst. product). With MgMeI in $(\text{iso-C}_5\text{H}_{11})_2\text{O}$ at room temp., (I) gives 1 CH_4 . Formation

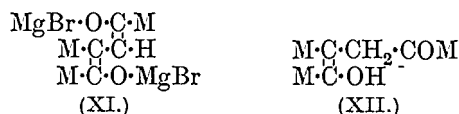


of (III) as above is indicated by interaction with Br- or I-EtOH to give $\text{COM}\cdot\text{CHM}\cdot\text{CH}(\text{Hal})\cdot\text{COM}$ (A-isomerides; cf. below), by failure to undergo oxidation when hydrolysed in presence of I or p - $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ to (VI) (below), and by further enolisation as described below. HCl in boiling AcOH containing a little H_2O or, less well, HI (*d* 1.7) at 160 — 170° , or HI-red P-I in boiling AcOH, but not Ac_2O - H_2SO_4 , converts (I) into 2 : 3 : 5-trimesitylfuran (IV), m.p. 106.5° [amorphous *Br*₄, m.p. 120 — 150° , and (? 4-)- NO_2 -derivative, m.p. 206.5 — 207° , obtained by HNO_3 -AcOH without oxidation occurring]. Decomp. of (III) [prep. from (I) by 2 MgMBr] by I-EtOH at 0 — 10° gives 74—79% of γ -iodo- $\alpha\beta\delta$ -trimesityl-*n*-butane- $\alpha\delta$ -dione-A (V), m.p. 213° (decomp.) [with small amounts of the B-isomeride (cf. below)], reduced to (I) by KI-AcOH at room temp., Zn dust in boiling AcOH, NaHSO_3 in boiling EtOH, or H_2 -PtO₂ in EtOAc, and converted by KOH (not NaOAc) in boiling EtOH into $\alpha\beta\delta$ -trimesityl- Δ^8 -butene- $\alpha\delta$ -dione (VI) (90%), m.p. 142 — 144° , which does not give a furan by Ac_2O - H_2SO_4 . With an excess of MgRHal (R = Ph, Et, or Me) at room temp., (I) gives the Mg mono-enolate-B (VII), which with I-EtOH at -60° gives γ -iodo- $\alpha\beta\delta$ -trimesityl-*n*-butane- $\alpha\delta$ -dione-B, m.p. 178° (reaction at -10° to -15° gives also some A-isomeride), converted by NaHSO_3 into (I) and by KOH into (VI) and giving (I) after short or (I) + (VI) after longer reaction with MgEtBr at 20°

(MgPhBr causes complete dienolisation). Interaction of (III)- MgEtBr (2 equivs.)- Et_2O at 0° with Br-EtOH at 20° gives mainly γ -bromo- $\alpha\beta\delta$ -trimesityl-*n*-butane- $\alpha\delta$ -dione-A, m.p. 192.5 — 193.5° ; at -60° (VII) gives similarly an isomeric *Br*-diketone-B, m.p. 230 — 231° ; other conditions yield mixtures. Both Br-diketones are converted by MgEtBr , followed by I-EtOH, into (V), by reduction into (I), and by KOH into (VI). Interaction of (V) with MgPhBr (3—4 equivs.) in Et_2O at 20° is the best source of (III). The free enols corresponding with (III) and (VII) ketonise as soon as formed. Boiling (II) and MgMBr in Pr^t_2O - N_2 for 2 hr. or (IX) (below) and MgPhBr in Et_2O for 0.5 hr. give the dienolate-A (VIII), converted by I-EtOH into (VI), by boiling AcOH into (I), or by boiling AcOH in absence of Mg salts into



the α -mono-enol-A, α -hydroxy- $\alpha\beta\delta$ -trimesityl- Δ^8 -butene- δ -one (IX), anhyd., m.p. 131 — 131.5° , and $+x\text{H}_2\text{O}$, double m.p. 95 — 100° (effervescence) and 130° , also obtained (60% yield) from (VI) by Zn dust in boiling AcOH. (IX) gives no colour with FeCl_3 , does not react with Br-EtOH or CH_2N_2 , reacts readily with 1 MgMeI or MgPhBr (for reaction with 2 MgPhBr cf. above), with red P-I-AcOH gives (IV), and with boiling KOH-95% EtOH gives (I). When (VIII) in Et_2O is treated at 0° with 80% EtOH containing 10% of AcOH and then with H_2O , the free dienol, $\alpha\beta\delta$ -trimesityl- Δ^8 -butadiene- $\alpha\delta$ -diol (X), m.p. 72 — 73° , is obtained. This is oxidised, when solid, by air to (VI), yields with MgMeI 1.89 CH_4 , and is rearranged to (I) by hot HCl-AcOH. Enolisation of (III) by hot MgPhBr - Et_2O (30 min.) or interaction of (V) with hot MgPhBr - Et_2O (5 min.) gives the dienolate-B (XI), which differs from (VIII) by being sol. in Et_2O .



I-EtOH converts (XI) into (VI), and boiling AcOH gives (IV); cold, dil. AcOH gives the oily α -mono-enol-B (XII), the precursor of (IV) in the preceding reaction. The possibility of formation of a Mg dienolate-C is discussed. M.p. are corr. R. S. C.

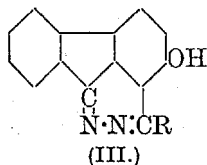
Condensations of cyclanones. R. POGGI (Atti X Congr. Internaz. Chim., 1938, III, 298—302, and Gazzetta, 1940, **70**, 265—269).— p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ (I) and 4-methylcyclohexanone in 4% aq. KOH give 2-*p*-tolylidene- (II), m.p. 67 — 68° (softens 65°) {*semi*-carbazone, m.p. 212 — 213° (decomp.); *oxime*, m.p. 108 — 112° (softens 105°) [Bz derivative, m.p. 115° (softens 112°)]}, with some 2 : 6-di-*p*-tolylidene-4-methylcyclohexanone, m.p. 135° (softens 131°), also obtained from (I) and (II). The two products are separated (from EtOH solution) with great difficulty. 6-Benzylidene-, m.p. 98 — 100° (softens 95°), and 6-*p*-anisylidene-2-*p*-tolylidene-4-methylcyclohexanone, m.p. 137 — 139° (softens 135°), are prepared from (II) and the appropriate aldehyde. E. W. W.

Alicyclic compounds. V. Syntheses of β -keto-amines from 2-, 3-, and 4-methylcyclohexanone. F. PIRONE (Atti X Congr. Internaz. Chim., 1938, III, 276—282).—2-Methylcyclohexanone with PhCHO (I) and NH_2Ph (II) gives its 6-CHPh derivative (III), and 2-methyl-2- α -anilinobenzylcyclohexanone, m.p. 118.5° (oxime, m.p. 208.5°; semicarbazone, m.p. 192°; picrate, m.p. 114—115°), which with NaOH and CHCl_3 gives PhNC odour, and with hot dil. acids gives some (III). 3-Methylcyclohexanone with (I) and $\text{NH}_3\text{-EtOH}$ (IV) gives its 6-CHPh derivative, new m.p. 47—49°, and with (I) and (II) gives this and 3-methyl-6(or 2)- α -anilinobenzylcyclohexanone, m.p. 164—165° [oxime, m.p. 185—186° (impure); semicarbazone, m.p. 185°], with a small amount of the 2(or 6)- α -anilinobenzyl isomere, m.p. 125—126°. 4-Methylcyclohexanone with (I) and (IV) gives its 2:6-(CHPh) $_2$ derivative, and with (I) and (II) gives this and 4-methyl-2- α -anilinobenzylcyclohexanone, m.p. 151—152° [oxime, m.p. 167—168° (impure)]. E. W. W.

Cyclanic polyalcohols. H. GAULT [with J. STECKL and J. SKODA] (Atti X. Congr. Internaz. Chim., 1938, III, 162—167).—An account of work already published (A., 1938, II, 411, 444). The by-product, m.p. 155°, obtained with hydroxymethylcyclohexanones from CH_2O and cyclohexanone, is now formulated as $\text{C}_{14}\text{H}_{22}\text{O}_3$ (cf. *loc. cit.*, 444).

E. W. W.

Structure of fluorene. E. BERGMANN and T. BERLIN (J. Amer. Chem. Soc., 1940, 62, 316—317).—Lability of the ethylenic linkings of fluorene (Lothrop, A., 1939, II, 502) is confirmed. 2-Acetoxy-fluorene (I) and -fluorenone are converted by AlCl_3 in PhNO_2 at 80° into 2-hydroxy-1-acetyl-fluorene, m.p. 159°, and -fluorenone (II), m.p. 206°, respectively. At 115° (I) gives a compound, $\text{C}_{15}\text{H}_{12}\text{O}_3$, m.p. 249°. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and (II) in hot EtOH give a pyridazine (III) (R = Me), m.p. 197° (decomp.); a similar compound (R = Ph), m.p. 181°, is obtained from 1-benzoylfluorenone. 2-Allyloxyfluorenone, m.p. 84—85°, when heated at 200° and then distilled at 0.05 mm., gives a mol. compound, m.p. 125—126°, of 2-hydroxy-1- and -3-allylfluorenone, reduced [$\text{H}_2\text{-Pd(OH)}_2$; boiling PrOH] to a separable mixture of 2-hydroxy-1- and -3-n-propylfluorenone, m.p. 202° and 155°, respectively or vice versa. R. S. C.



Action of acetic anhydride on acenaphthenone. (SIGNA.) E. GHIGI (Atti X Congr. Internaz. Chim., 1938, III, 168—178).—The substance, m.p. 117° (A., 1938, II, 327), obtained by hydrolysis of 8-acetoxy-7-acetyl- is 8-hydroxy-7-acetyl-acenaphthylene (I) (benzoate, m.p. 148—149°). PhN_2Cl with (I) gives acenaphthenequinonemonophenylhydrazine. With $\text{NaOH-MeOH-Me}_2\text{SO}_4$, (I) gives only its Na salt, m.p. 260°; it is unaltered by EtBr or PhNCO. (I) gives a phenylhydrazone, m.p. 196—198°, an oxime, m.p. 201—203°, and a semicarbazone, m.p. 235—236° (decomp.). With $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$, (I) gives 1:8- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$, also obtained using $\text{NaOH-H}_2\text{O}_2$, or, with a substance, m.p. 215°, using $\text{KMnO}_4\text{-NaOH}$. When distilled with Zn, (I) gives acenaphthene; with

quinoline and Cu, some acenaphthenone and resins are formed; with 20% NaOH (I) gives bisacenaphthylidenone, also obtained when MeOH-HCl is used.

E. W. W.

β -Diketones. A. BANCHETTI (Gazzetta, 1940, 70, 134—144).—An attempt is made to prepare 3-methyl-5:6-benzo-indone. $2\text{-C}_{10}\text{H}_7\text{Ac}$ (I) and EtOAc with Na or NaNH_2 give 2-naphthoylacetone (II), m.p. 81.5—82.5°, which with NHPh-NH_2 gives a pyrazolone. With 82% H_2SO_4 at 60—65°, (II) does not cyclize; prolonged heating at 70° gives $\text{H}_2\text{O-sol.}$ (sulphonated?) products. Using 89% H_3PO_4 , only (I) is isolated. 10% NaOH yields (I) and $\beta\text{-C}_{10}\text{H}_7\text{-CO}_2\text{H}$, also obtained by KMnO_4 oxidation. EtOBz and (I) give ω -2-naphthoylacetophenone (III), m.p. 101—102°, similarly unchanged by H_2SO_4 . $1\text{-C}_{10}\text{H}_7\text{Ac}$ and Na in EtOAc give impure 1-naphthoylacetone (IV), b.p. 205—210°/20 mm., which is converted by NaOH and by KMnO_4 into $\alpha\text{-C}_{10}\text{H}_7\text{-CO}_2\text{H}$ and by 82% H_2SO_4 at 60—65° into $1:8\text{-C}_{10}\text{H}_6\text{<C(Me)=CO>CH}$ (cf. Criegee *et al.*, A., 1933, 1272). (II) and (III) are found by Hieber's method to be 97—100% enol in the solid state, and (IV) to be 92% enol. Directions of enolisation and condensation are discussed. E. W. W.

Synthesis of polycyclic compounds. I. 1':2':3':4'-Tetrahydro-1:2-benzanthrone-9. N. G. TSCHERNOVA and B. M. MICHAÏLOV (J. Gen. Chem. Russ., 1939, 9, 2168—2170).—6-o-Carboxybenzyl-1':2':3':4'-tetrahydronaphthalene with ZnCl_2 at 180°/45 min. yields chiefly 2:3-tetramethylenecanthranol, together with 1':2':3':4'-tetrahydro-1:2-benzanthrone-9, m.p. 109—109.7°; the latter and MgMel give 9-methyl-1':2':3':4'-tetrahydro-1:2-benzanthracene, m.p. 122.6—124.2° (picrate, m.p. 125.5—126.2°). R. T.

Steroid ketones.—See B., 1940, 324,325.

Sterols. LXXXVII. Cholesterol and sitosterol derivatives. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 516—517).— KMnO_4 in $\text{AcOH-H}_2\text{O}$ (proportions detailed for each case) at room temp. or 55° converts cholesterol into cholestan-5-ol-3:6-dione (I), m.p. 248—251° (probably that obtained by CrO_3 following alkaline KMnO_4), cholesteryl acetate into 3-acetoxycholestan-5-ol-6-one, m.p. 231—233° (oxime, m.p. 204—206°), neocholestene into cholestane-2:3-dicarboxylic acid (II), m.p. 193—195°, cholestan-3(β)-ol into (II) and cholestanone (sole product at room temp.), sitosterol into a OH-diketone, $\text{C}_{29}\text{H}_{48}\text{O}_3$, m.p. 240°, and sitosteryl acetate into a CO-diol acetate, $\text{C}_{31}\text{H}_{52}\text{O}_4$, m.p. 251°. KHSO_4 at 150—180° dehydrates (I) to $\Delta^{4:5}$ -cholestene-3:6-dione, m.p. 121—123°. Sitosteryl chloride and $\text{CrO}_3\text{-AcOH}$ at 55° give 7-keto- (III), m.p. 155—156°, reduced by $\text{Al(OPr}^i)_3\text{-Pr}^i\text{OH}$ to 7-hydroxy-sitosteryl chloride, m.p. 138—139°; (III) and KOH in boiling 90% EtOH give 7-ketositosterylene, m.p. 106—107°. $\text{H}_2\text{-PtO}_2$ at 3 atm. in Et_2O reduces (III) to 7-ketositostyl chloride, m.p. 128—129°, stable to CrO_3 at 60° and further hydrogenated in AcOH to sitostyl chloride. R. S. C.

Partial synthesis of corticosterone. I. P. N. CHAKRAVORTY and E. S. WALLIS (J. Amer. Chem.

Soc., 1940, 62, 318—320).—3-Hydroxy-12-ketocholanic acid (I) (Me ester, m.p. 143°), readily obtained by oxidation of deoxycholic acid (Kaziro *et al.*, A., 1937, II, 500), gives an acetate, m.p. 197°, which with Br-HBr-AcOH at 70° and then at room temp. gives a gummy 11-Br-derivative. NaOEt-EtOH (not NaOAc-AcOH) converts this into 3-hydroxy-12-keto- $\Delta^9:11$ -cholenic acid (II) (30%), m.p. 172—173° (absorption max. at 2425 Å.), but Zn-AcOH affords (I). The readily formed, crude semicarbazone, m.p. 221°, of (II) with NaOEt-EtOH at 180° gives α -3-hydroxy- $\Delta^9:11$ -cholenic acid, m.p. 183—184°, $[\alpha]_D^{25} + 27.0^\circ$ in abs. EtOH, with a small amount of the β -epimeride. R. S. C.

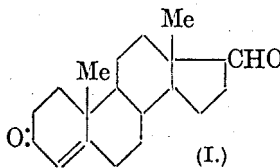
Steroids. XXIV. $\Delta^4:6$ -3-Ketones of the androstane and pregnane series. A. WETTSTEIN [with, in part, H. FREY] (Helv. Chim. Acta, 1940, 23, 388—399).— Δ^5 -Androstene-3t: 17t-diol 17-mono-benzoate (I) and *p*-benzoquinone (II) are mixed with PhMe, part of which is removed in a vac. The residual solution when boiled for $\frac{3}{4}$ hr. with $\text{Al}(\text{OBU}^\gamma)_3$ gives 6-dehydrotestosterone benzoate (III), m.p. 257—260°, hydrolysed to 6-dehydrotestosterone, m.p. 209—211° (acetate, m.p. 143—144°). Similarly, Δ^5 -pregnen-3-ol-2-one affords 6-dehydroprogesterone, m.p. 147—148°, $[\alpha]_D^{25} + 149.5^\circ$ in EtOH, and Δ^5 -21-acetoxypregnen-3-ol-20-one yields 6-dehydrodeoxycorticosterone acetate, m.p. 115—116°, $[\alpha]_D^{25} + 151.5^\circ$ in EtOH. Δ^5 -Androstene-17t-ol-3-one benzoate, m.p. 178—181°, obtained in >60% yield by successive bromination, oxidation, and debromination of (I), is converted by (II) and $\text{Al}(\text{OBU}^\gamma)_3$ into (III) and is partly oxidised by (II) alone. Oxidation of 3-androstane-3t: 17t-diol 17-hexahydrobenzoate with (II) and $\text{Al}(\text{OBU}^\gamma)_3$ leads to a gelatinous product, hydrolysed to dihydrotestosterone, m.p. 179—181°. Reaction does not consist in dehydrogenation of OH at C₃, followed by displacement of the original double linking and dehydrogenating introduction of a new double linking, since (III) is not obtained by treating testosterone benzoate with (II) and $\text{Al}(\text{OBU}^\gamma)_3$ or with (II) alone. The introduction of the second double linking must occur at latest in the Δ^5 -3-ketone stage. M.p. are corr. H. W.

Preparation of 17-methyltestosterone from dehydroandrosterone. A. D. TSCHINAIEVA, M. I. USCHAKOV, and A. T. MARTSCHEVSKI (J. Gen. Chem. Russ., 1939, 9, 1865—1867).—Oxidation (Oppenauer) of 17-methylandrosterone-3: 17-diol gives 17-methyltestosterone in 40% yield. The product is best purified by chromatographic adsorption on Al_2O_3 . R. T.

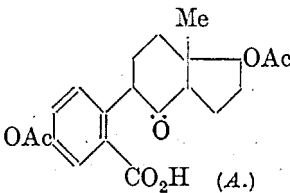
Oxidation of cholesteryl acetate dibromide to trans-dehydroandrosterone, and conversion of the latter into methyltestosterone. G. I. KIPRIANOV and B. E. FRENKEL (J. Gen. Chem. Russ., 1939, 9, 1682—1686).—Optimum conditions for oxidation (CrO_3) of cholesteryl acetate dibromide (I) by Butenandt's method (A., 1936, 77) are: (I) 36 g., AcOH 1600 ml., H_2O 40 ml., H_2SO_4 11.2 ml., and NH_4VO_3 1 g. (4 hr. at 50°); the yield of trans-dehydroandrosterone (II) (as semicarbazone) is 4%. (II), which need not be purified, is converted into 17-methylandrosterone-3: 17-diol (whence 17-methyl-

testosterone) by Ruzicka's method (*ibid.*, 76), using a tenfold excess of MgMeI . R. T.

Steroids. XXV. Homologues of the testicular hormone. II. 20-Norprogesterone. K. MIESCHER, F. HUNZIKER, and A. WETTSTEIN (Helv. Chim. Acta, 1940, 23, 400—404).— Δ^4 -Pregnene-20 α : 21-diol-3-one is oxidised by HIO_4 in aq. dioxan at room temp. to Δ^4 -17-aldehydroandrosten-3-one [20-norprogesterone] (I), m.p. 151—153°, $[\alpha]_D^{25} + 158.5^\circ$ in dioxan (disemicarbazone, decomp. 296°), slowly oxidised by air in AcOH at $\sim 80^\circ$ to Δ^4 -3-keto α ti cholonic acid, m.p. 256—260°. M.p. are corr. (vac.). H. W.



Estrogens with oxygen in ring B. III. 6-Keto- α -estradiol. B. LONGWELL and O. WINTERSTEINER (J. Biol. Chem., 1940, 133, 219—229).—The ketonic fraction (isolated by Girard reagent T) obtained by oxidation [CrO_3 ($\equiv 4.5 \text{ O}$) in AcOH at 23—24°] of α -estradiol diacetate contains 6-keto- α -estradiol (I), m.p. 281—283° (slight decomp.), $[\alpha]_D^{25} + 4.2^\circ$ in EtOH, [semicarbazone, m.p. 280—310° (decomp.)], and its diacetate, m.p. 173—175°. From the acidic oxidation products is isolated a ketodiacyetoxy-acid, $\text{C}_{21}\text{H}_{24}\text{O}_7$, m.p. 144—145°, probably (A), converted by Ac_2O -NaOAc into an enol-lactone, $\text{C}_{21}\text{H}_{22}\text{O}_6$, m.p. 152—153°.

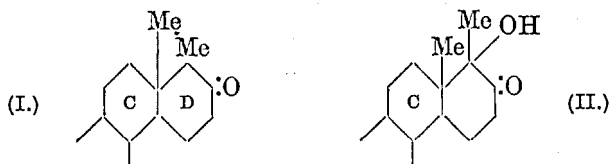


The oestrogenic potency of (I) is a quarter of that of estradiol. M.p. are corr. J. D. R.

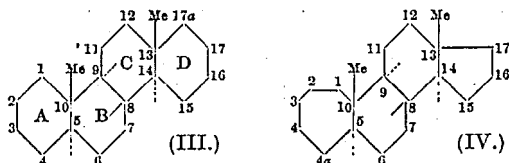
Preparation of Δ^5 -pregnene-3: 17-diol-20-one from Δ^5 -17-acetylenylandrosterone-3: 17-diol. H. E. STAVELY (J. Amer. Chem. Soc., 1940, 62, 489—491).—17-Acetylenyl- Δ^5 -androsterone-3: 17-diol, NH_2Ph , HgO (or, better, HgCl_2), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at room temp. (1 week) give 20-anilo- Δ^5 -pregnene-3: 17-diol (I), m.p. 148°, $[\alpha]_D^{25} - 196 \pm 2^\circ$ in CHCl_3 (cf. Goldberg *et al.*, A., 1939, II, 552) (3-acetate, m.p. 232—234°, $[\alpha]_D^{25} - 176 \pm 2^\circ$ in CHCl_3), which in aq. MeOH is equilibrated with Δ^5 -pregnene-3: 17-diol-20-one (II), sinters at 158°, m.p. 161—163° (3-acetate oxime, m.p. 254—256°). Bromination, CrO_3 -AcOH (first at room temp. and then at 45°), and then Zn dust converts the 3-acetate, m.p. 196—198°, $[\alpha]_D^{25} - 61 \pm 1.5^\circ$ in CHCl_3 , of (II) into 3-acetoxydehydroandrosterone (isolated as semicarbazone), and 3% KOMe-MeOH hydrolyses and rearranges it to 4: 10-dihydroxy-3-keto-4: 2a: 12a-trimethyl- Δ^8 -hexadecahydrochrysene (Ruzicka *et al.*, A., 1939, II, 76, 327), now termed Δ^5 -chrysopregnene-3: 17-diol-18-one. Only members of the 3(α) series undergo this rearrangement. Acid hydrolysis of (I) causes a different rearrangement. R. S. C.

Steroids and sex hormones. LIX. Constitution of the hexadecahydrochrysene derivatives formerly known as "neopregnene compounds." L. RUZICKA and H. F. MELDAHL (Helv. Chim. Acta, 1940, 23, 364—375; cf. A., 1939, II, 218, 327; Miescher *et al.*, *ibid.*, 166).—Compounds of the neopregnene series are constituted in accordance

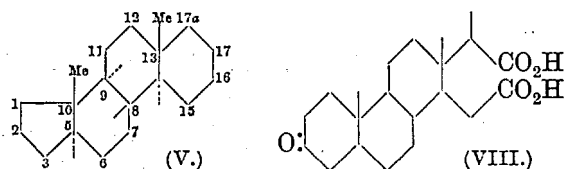
with (I) and the α -OH-ketones (from which they are derived) obtained by hydration of 17-hydroxy-17-



acetylenyl derivatives of the androstane and androstene series have probably the structure (II). The saturated compounds of the two series are therefore derivatives of perhydrochrysene and the neopregnene compounds are hexadecahydrochrysene derivatives. It is proposed to designate compounds formed by ring-enlargement with the prefix "homo" and the letter indicating the ring which has suffered enlargement. Ring contraction is indicated by the prefix "nor." Thus (III), (IV), and (V) are named respectively D-homoandrostane, A-homoandrostane, and



A-nor-D-homoandrostane. Hydrogenation (PtO_2 in AcOH) of Δ^5 -3-trans-acetoxy-17a-methyl-D-homoandrost-17-one (neopregnenolone acetate) (VI) affords 3-trans-acetoxy-17a-methyl-D-homoandrost-17-one (VII), m.p. 174—175°, hydrolysed by K_2CO_3 in boiling $\text{MeOH-H}_2\text{O}$ to the 3-hydroxy-compound, m.p. 222—224°, which is oxidised by CrO_3 in AcOH to 17a-methyl-D-homoandrostane-3:17-dione, m.p. 200—202°; the corresponding hydrazone, decomp. $>320^\circ$, is transformed by Na and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in amyl alcohol at 200° into 17a-methyl-D-homoandrostane, m.p. 108—109°, $[\alpha]_D^{25} -3^\circ \pm 1^\circ$ in dioxan. isoAmyl formate, (VII), and NaOEt in Et_2O yield 3-trans-hydroxy-17a-methyl-16-hydroxymethylene-D-homoandrost-17-one,



m.p. 168—170°, oxidised by CrO_3 in AcOH at room temp. to the ketodicarboxylic acid (VIII), m.p. 219—220° [Me_2 ester, m.p. 124—126°; anhydride, m.p. 188—191°, which passes at 200°/50 mm. into an (impure) substance, $\text{C}_{30}\text{H}_{30}\text{O}_2$, m.p. 124—127°]. Absorption (PtO_2 in AcOH) of 2 H_2 by (VI) and subsequent hydrolysis with K_2CO_3 leads to 3-trans-17-dihydroxy-17a-methyl-D-homoandrostane, m.p. 180—200° (probably a mixture of isomerides) (diacetate, m.p. 186—187°), dehydrogenated (Se at 345—350°) to 1-methylchrysene, m.p. 253—254° [additive compound with $\text{C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 174—175°]. All m.p. are corr. (vac.). H. W.

Steroids and sex hormones. LX. Transformation of cyanohydrins of the androstane series into ketones of the perhydrochrysene

series. M. W. GOLDBERG and R. MONNIER (Helv. Chim. Acta, 1940, 23, 376—384).—A method for the enlargement of ring D of androstane derivatives is described. *trans*-Dehydroandrost-17-one cyanohydrin is hydrogenated (PtO_2 in AcOH at 70°) to 3-*trans*-17-dihydroxy-17-aminomethyl-androstane (I), m.p. 222—225°, $[\alpha]_D^{25} -16.5^\circ \pm 1^\circ$ in *N*-AcOH (Ac_3 derivative, m.p. 166°). More advantageously (I) is obtained by reduction of *trans*-dehydroandrost-17-one cyanohydrin 3-monoacetate to the corresponding acetoxy-acetate (II), m.p. $\sim 235^\circ$ (decomp.), which is then hydrolysed. Analogously androst-17-one cyanohydrin is converted into 3-*epi*-17-dihydroxy-17-aminomethyl-androstane (III), m.p. 204—206°, $[\alpha]_D^{25} +4.5^\circ \pm 1.0^\circ$ in *N*-AcOH (Ac_2 derivative, m.p. 207—208°). Treatment of the acetate of (I) with NaNO_2 and aq. AcOH leads to 3-*trans*-hydroxy-D-homoandrost-17a-one (IV), m.p. 193—195°, $[\alpha]_D^{25} -66.5^\circ \pm 1^\circ$ in MeOH [semicarbazone, m.p. 252—254°; Ac derivative, m.p. 124—125°, also obtained from (II) and HNO_2]. The acetate of (III) is similarly transformed into 3-*epi*-hydroxy-D-homoandrost-17a-one, m.p. 203—205°, $[\alpha]_D^{25} -35.5^\circ \pm 1.5^\circ$ in MeOH (semicarbazone, m.p. 233—235°; Ac derivative, m.p. 150—151°, $[\alpha]_D^{25} -21.7^\circ \pm 1^\circ$ in MeOH). (IV), is converted by MgMeI in $\text{Et}_2\text{O-C}_6\text{H}_6$ into 3-*trans*-17a-dihydroxy-17a-methyl-D-homoandrostane, which after treatment with Girard's reagent *T* is dehydrogenated (Se at 350°) to 1-methylchrysene, m.p. 253—254° [additive compound, m.p. 173—175°, with $\text{C}_6\text{H}_3(\text{NO}_2)_3$]. All m.p. are corr. H. W.

Synthesis of substituted 1:4-naphthaquinones. C. F. KOELSCH and D. J. BYERS (J. Amer. Chem. Soc., 1940, 62, 560—562).— $\text{o-C}_6\text{H}_4(\text{CO}_2\text{Et})_2$, Na, and $\text{Pr}^\circ\text{CO}_2\text{Et}$ give 2-ethylindane-1:3-dione, m.p. 53—55° (lit. 55.5°), b.p. 135—140°/7 mm., which with $\text{CH}_2\text{Br-CO}_2\text{Et}$ and KOH-EtOH gives *Et* 1:3-diketo-2-ethyl-2-indanylacetate, m.p. 77—78.5°, converted by NaOEt-EtOH-H_2 into 3-carbethoxy-2-ethyl-1:4-naphthaquinol, m.p. 110.5—111°. With CrO_3 -AcOH this gives 3-carbethoxy-2-ethyl-1:4-naphthaquinone, m.p. 47.5—48°, with O_2 in NaOH-EtOH at 50° gives 3-hydroxy-2-ethyl-1:4-naphthaquinone, and with a little EtOH in boiling aq. NaOH and H_2 gives 2-ethyl-1:4-naphthaquinone. Similarly are obtained 2-methyl-, 2-*n*-propyl-, m.p. 48—49.5° (lit. 50.5°), and 2-*n*-butyl-indane-1:3-dione, m.p. 35° (lit. 33°), b.p. 155—160°/1 mm., *Et* 1:3-diketo-2-methyl-, m.p. 91—92° (lit. 161—162°), 2-*n*-propyl-, an oil, and 2-*n*-butyl-2-indanylacetate, an oil, 3-carbethoxy-2-methyl-, m.p. 100—101°, 2-*n*-propyl-, m.p. 125—126.5°, and 2-*n*-butyl-1:4-naphthaquinol, m.p. 98.5—100°, 3-carbethoxy-2-methyl-, m.p. 99—100°, and 3-hydroxy-2-*n*-butyl-1:4-naphthaquinone, m.p. 100—101° (lit. 101—101.5°). R. S. C.

Vitamin-K activity of naphthaquinones. E. FERNHOLZ, S. ANSBACHER, and H. B. MACPHILLAMY (J. Amer. Chem. Soc., 1940, 62, 430—432).—The vitamin-K activity of numerous alkyl-1:4-naphthaquinones is recorded. The 2-Me derivative is the most active. $n\text{-C}_{15}\text{H}_{31}\cdot\text{COCl}$, tetrahydronaphthalene, and AlCl_3 in CS_2 give 5:6:7:8-tetrahydro-2-naphthyl $n\text{-C}_{15}\text{H}_{31}$ ketone, m.p. 44—45°, reduced (Clemmensen-Mikeska) to 2-*n*-hexadecyl-5:6:7:8-tetrahydro-

naphthalene, b.p. 210—215°/~1 mm., which with S at 200—210° gives 2-*n*-hexadecylnaphthalene, m.p. 45—46°. CrO_3 -AcOH then gives 2-*n*-hexadecyl-1:4-naphthaquinone, m.p. 80—81°. 2-*n*-Octadecyl-1:4-naphthaquinone, m.p. 84—85°. 3-methyl-5:6:7:8-tetrahydro-2-naphthyl $\text{C}_{17}\text{H}_{35}$ ketone, m.p. 64—65°, 2-methyl-3-*n*-octadecyl-5:6:7:8-tetrahydronaphthalene, m.p. 60—61°, -*naphthalene*, m.p. 47—48°, and 1:4-naphthaquinone, m.p. 95—97°, are also prepared.

R. S. C.

General method of preparing 2-methyl-3-alkylnaphthaquinones. Constitution and vitamin-K activity. P. KARRER and A. EPPRECHT [with, in part, H. KÖNIG] (Helv. Chim. Acta, 1940, 23, 272—283).—Gradual addition of AcCl and 2-methyl-5:6:7:8-tetrahydronaphthalene in CS_2 to AlCl_3 in CS_2 affords 3-acetyl-2-methyl-5:6:7:8-tetrahydronaphthalene, b.p. 156—157°/11 mm., reduced (Clemmensen) to 2-methyl-3-ethyl-5:6:7:8-tetrahydronaphthalene, b.p. 127—128°/11 mm., which is dehydrogenated (S at 210—220°) to 2:3- $\text{C}_{10}\text{H}_6\text{MeEt}$ (I). This is oxidised (CrO_3 in AcOH) to 2-methyl-3-ethyl-1:4-naphthaquinone, m.p. 73° (some 5:8-quinone appears to be formed simultaneously). 3-Acetyl-2-methylnaphthalene, b.p. 164°/11 mm., is converted by successive treatment with PCl_5 and KOH-EtOH at 125° into 2-methyl-3-acetylenylnaphthalene, m.p. 81°, hydrogenated to (I). 3-Stearyl-2-methyl-5:6:7:8-tetrahydronaphthalene, m.p. 64°, is reduced (Clemmensen) to 2-methyl-3-octadecyl-5:6:7:8-tetrahydronaphthalene, m.p. 64°; this is dehydrogenated to 2-methyl-3-octadecylnaphthalene (impure), which is oxidised to 2-methyl-3-octadecyl 1:4-naphthaquinone, highest observed m.p. 100°, the purity of which is established by potentiometric titration with Na_2 dithionite. $\zeta\kappa\xi$ -Trimethylpentadecan- β -one, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn-Cu in PhMe at 100—115° give *Et* β -hydroxy- $\beta\zeta\kappa\xi$ -tetramethylhexadecate, b.p. 179°/0.4 mm., which is converted by successive treatment with PBr_3 and KOH-EtOH into *phytenic acid*, b.p. 174°/0.4 mm., readily hydrogenated (Pt) to phytanic acid. The latter (obtained by oxidation of dihydrophytol by CrO_3 - KHSO_4 in 80% AcOH) is converted (SOCl_2) into the chloride, which is condensed to 3-phytanyl-2-methyl-5:6:7:8-tetrahydronaphthalene, b.p. 217—220°/0.04 mm. This gives 2-methyl-3-dihydrophytyl-5:6:7:8-tetrahydronaphthalene, dehydrogenated to 2-methyl-3-dihydrophytylnaphthalene, b.p. 212°/0.015 mm., oxidised to non-cryst. 2-methyl-3-dihydrophytyl-1:4-naphthaquinone possessing the same absorption spectrum as phyloquinone (vitamin- K_1).

It is suggested that vitamin- K_2 is a 2-methyl-1:4-naphthaquinone with a squalene or similar complex residue at C_{13} .

H. W.

Synthesis of vitamin- K_1 .—See A., 1940, III, 325.

Synthesis of condensed ring compounds. II. Reaction of $\Delta^{\alpha\gamma}$ -hexatriene with 1:4-naphthaquinone. L. W. BUTZ, E. W. J. BUTZ, and A. M. GADDIS (J. Org. Chem., 1940, 5, 171—183).— $\Delta^{\alpha\gamma}$ -Hexadien- γ -ol (prep. from $\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$ and $\text{CH}_2=\text{CH}\cdot\text{CHO}$ detailed) is dehydrated [$\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and a little quinol at 130—200°] to $\Delta^{\alpha\gamma}$ -hexatriene (I), b.p. 80—82°/757 mm., which may contain ~30% of $\Delta^{1:3}$ -cyclohexadiene (II) [this may arise from (I) or

by cyclodehydration of a rearrangement product such as $\Delta^{8:8}$ -hexadien- α -ol]. 1:4-Naphthaquinone and (I) in EtOH at 50°/6 hr. (sealed tube) thus give 27% of the 1:4-endoethylenetetrahydroanthraquinone (III), m.p. 134—136° [Diels *et al.*, A., 1929, 1303; prep. from (II); oxidised (air in EtOH-KOH) to 1:4-endoethylene-1:4-dihydroanthraquinone (IV), decomp. 187—188° (rapid heating) to anthraquinone and C_2H_4 (cf. *loc. cit.*)], and 70% of (probably) *cis*- + *trans*-1-vinyl-*cis*-1:4:4a:9a-tetrahydroanthraquinone (V), an oil, which is oxidised (air in EtOH-KOH at 30°) to 1-vinylnanthraquinone (VI), m.p. 163—164°. Ozonolysis of (VI) in AcOH, fission by boiling aq. AcOH, and oxidation (CrO_3 , aq. AcOH) of the resulting product, m.p. 167—169° (partly), gives anthraquinone-1-carboxylic acid. Reduction (H_2 , Pd-black, AcOH) of (VI) and oxidation (CrO_3) of the H_4 -derivative affords 1-ethylanthraquinone. No conversion of (V) into (III) occurs in EtOH at 50—55°/14 days. When (V) is heated at 200—236°/2.5 mm. for 1 hr., 10% of (?) 9:10-dihydroxy-1:4-endoethylene-1:4-dihydroanthracene, decomp. 147—150° [oxidised (EtOH- FeCl_3) to (IV)], 50% of (?) 1-vinyl-1:4-dihydroanthraquinone, m.p. 97—99° [oxidised (air in EtOH-KOH) to (VI)], and an oil are obtained. M.p. are corr.

H. B.

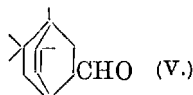
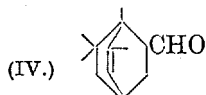
Biochemistry of the lower fungi. III. Pigment of *Penicillium citreo-roseum*, Dierckx. T. POSTERNAK and J. P. JACOB (Helv. Chim. Acta, 1940, 23, 237—242).—The isolation of *citreorosein* (I), $\text{C}_{15}\text{H}_{19}\text{O}_6$, m.p. 273—275° (decomp.) when slowly heated, is described. It contains 4 OH (Ac_4 , m.p. 187—188°, Bz_4 , m.p. 206—208° and 223° after resolidification, and Me_4 , m.p. 187—188°, derivatives). It does not afford AcOH when oxidised (Kuhn and Roth). When distilled with Zn dust it gives 2-methylantracene. (I) is sol. in solutions of alkali carbonates, gives a salt with 1 mol. of $\text{C}_5\text{H}_5\text{N}$, does not dye mordanted cotton, and very closely resembles emodin in absorption spectrum. (I) is therefore a 4:5:7-trihydroxy-2-hydroxymethylantraquinone. (Cf. A., 1940, II, 135.)

H. W.

Pyrolysis of pinene. I. Pyronenes. II. Formulæ of pyronenes. G. DUPONT and R. DULOU (Atti X Congr. Internaz. Chim., 1938, III, 123—129, 129—139).—I. Pyrolysis of *d*-pinene (I) in a Cu tube at 350° gives a product shown by Raman spectra to contain, with limonene and *allocymene*, isomeric α - (II), b.p. 43°/11 mm., $[\alpha]_D +17.18^\circ$, and β -pyronene (III), b.p. 48—50°/8 mm., $[\alpha]_D +4.52^\circ$, which are identified as 1:1:2:3-tetramethylcyclohexadienes, formed by rupture of the 4-carbon ring of (I). The Raman spectra of the tetrahydro- α - and β -pyronenes obtained (Pt- H_2) from (II) and (III) are identical with those of H_2 -derivatives of cyclogeraniolones obtained by Escourrou's method (cf. A., 1926, 1238), or by cyclising dihydromyrcene, geraniolene, or linalolene.

II. The following reactions show that (II) and (III) are 1:5:5:6- and 1:2:6:6-tetramethyl- $\Delta^{1:3}$ -cyclohexadiene, respectively. Diels-Alder condensation with $(:\text{C}\cdot\text{CO}_2\text{Me})_2$, followed by thermal decomp. of the product, gives, from (II), $\text{CHMe}\cdot\text{CMe}_2$ [with some $\text{CMe}_2\cdot\text{CH}_2$ probably derived from (III)] and 3:1:2-

$C_6H_3Me(CO_2H)_2$, and, from (III), $CMc_2:CH_2$ and 3:4:1:2- $C_6H_2Me_2(CO_2H)_2$. Naphthaquinone condenses with (II) to a compound, m.p. 123—124°, dehydrogenated and pyrolysed in presence of litharge to give 1-methylantraquinone (and $CHMe:CMc_2$). Similarly (III) gives a naphthaquinone additive compound, m.p. 95—96°, which on atm. oxidation of its EtOH solution, and pyrolysis, gives 1:2-dimethylantraquinone (and $CMc_2:CH_2$). With $CH_2:CH:CHO$, (III) gives a 50% yield of 1:2:2-trimethyl-1:4- α -methylvinylencyclohexane-5(or 6)-aldehyde [(IV) or (V)], b.p. 123°/15 mm. (semi-



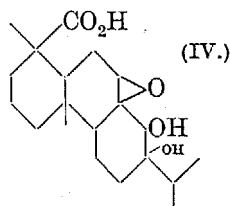
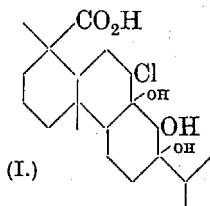
carbazone, m.p. 209—210°). (II) gives only 10% of an aldehyde (semicarbazone, m.p. ~204—205°). With maleic anhydride, (II) gives, after hydrolysis, 1:2:3:3-tetramethyl-1:4-vinylencyclohexane-5:6-dicarboxylic acid, m.p. 195°, whilst (III) gives 1:2:2-trimethyl-1:4- α -methylvinylencyclohexane-5:6-dicarboxylic anhydride, m.p. 154°. Hydrogenation of (II), using Raney Ni, gives a mixture of three, and that of (III) a mixture of two, tetramethylcyclohexenes, characterised by their Raman spectra. E. W. W.

Preparation of borneol glucuronide. H. K. MURER and L. A. CRANDALL, jun. (J. Amer. Chem. Soc., 1940, 62, 674—675).—The prep. is improved.

R. S. C.

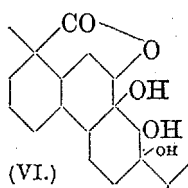
Homologues of the camphor group. XIII. Partial synthesis of 4-methylcamphor. S. S. NAMETKIN and A. P. STUKOV (J. Gen. Chem. Russ., 1939, 9, 2081—2084).—4-Methylcamphoric anhydride, distilled from an Al-Ni catalyst at 220°, yields 4-methylcampholide, m.p. 193—194°, which does not react with KCN or with HBr in AcOH, and therefore cannot serve for the synthesis of 4-methylcamphor (I) by Komppa's method (A., 1909, i, 110). The same applies to 4-methylcamphor-3-carboxylic acid, m.p. 134—134.5° (Et ester, b.p. 145.5—146°/9 mm.), prepared by passing CO_2 into a C_6H_6 solution of (I) and $NaNH_2$. 3-Aldehyde-4-methylcamphor in N-NaOH and NH_2OH , heated at 100°, yield 3-cyano-4-methylcamphor, m.p. 163—164°, which is heated with 50% KOH (6—8 hr. at the b.p.). The Ca salt of 4-methylhomocamphoric acid, m.p. 167—168°, so produced gives (I) when heated under reflux. R. T.

Diterpenes. XL. Isomeric tetrahydroxyabiatic acids and their functional transformation products. L. RUZICKA and L. STERNBACH (Helv. Chim. Acta, 1940, 23, 333—341; cf. A., 1938, II, 287).—Chlorotrihydroxyabiatic acid (I) is converted by a



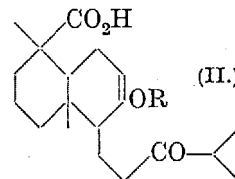
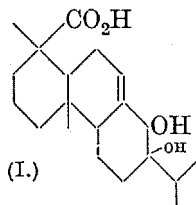
small excess of NaOH into a product (II), m.p. ~125—130°, $[\alpha]_D -53.1^\circ \pm 0.5^\circ$ in $CHCl_3$, which is

separated by $COMe_2$ into γ -tetrahydroxyabiatic acid (III), m.p. 130° to 150° according to the rate of heating, $[\alpha]_D -29.5^\circ \pm 0.4^\circ$ to $-61.5^\circ \pm 0.4^\circ$ in MeOH in three weeks, and oxidodihydroxyabiatic acid (IV), m.p. 130—150°, $[\alpha]_D -52.3^\circ \pm 1^\circ$ in MeOH. (III) is transformed by HCl into (I) and α -tetrahydroxyabiatic acid (V). (IV) is very unstable; it yields a highly chlorinated product with dil. HCl and is slowly transformed by boiling $COMe_2-2N-H_2SO_4$ into (V), m.p. 249—250°, $[\alpha]_D -39.8^\circ$. Boiling PhMe converts (I)



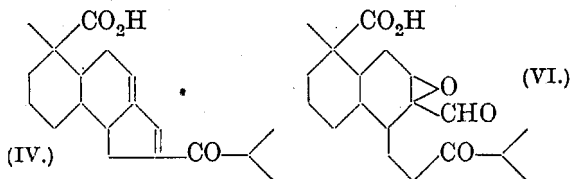
into tetrahydroxyabietolactone (VI), m.p. >330°, $[\alpha]_D -77^\circ \pm 1.5^\circ$ in $CHCl_3$, which does not react with HCl or boiling $COMe_2-2N-H_2SO_4$, is unaffected by NH_2OH , $NH_2 \cdot CO \cdot NH \cdot NH_2$, or CH_2N_2 , is not hydrogenated (PtO_2), is indifferent to boiling 0.5N-KOH-EtOH, but is hydrolysed by 35% KOH at 160° to (V). Slow evaporation of a very dil. solution of (IV) in $COMe_2$ gives β -tetrahydroxyabiatic acid, m.p. 151° (softening at 127°) (m.p. depends greatly on rate of heating), $[\alpha]_D -67.7^\circ \pm 0.4^\circ$ in MeOH ($c = 2.5$) (Me ester, m.p. 70—100°), which is not transformed into a halogenated product by cold HCl but yields (V) with boiling dil. H_2SO_4 . Oxidation of (V) with $Pb(OAc)_4$ in AcOH or KIO_4 in MeOH-2N- H_2SO_4 gives ketotrihydroxyabiatic acid, m.p. 204—205°, $[\alpha]_D +7.0^\circ \pm 0.4^\circ$ (as Na salt in H_2O), identical with the "isomeric tetrahydroxyabiatic acid" (*loc. cit.*). All m.p. are corr. H. W.

Diterpenes. XLI. Degradation of dihydroxyabiatic acid and of oxidodihydroxyabiatic acid. L. RUZICKA and L. STERNBACH (Helv. Chim. Acta, 1940, 23, 341—355).—Dihydroxyabiatic acid (I) [reasons are advanced for its formulation as in (I)] (Me ester, m.p. 106—107°) is oxidised by $o-CO_2H \cdot C_6H_4 \cdot CO_2H$ to α -tetrahydroxyabiatic acid. (I) is oxidised by $Pb(OAc)_4$ (1 mol.) in AcOH to the amorphous ketoaldehydic acid [(II), R = CHO], characterised by the cryst. dioxime, m.p. 188.5—189.5° (block preheated to 182°), and the dicarboxylic acid (III) [(II), R = CO_2H], m.p. 212—212.5° [oxime, m.p. 227—229° after becoming yellow at 217° (block preheated to 213°)]. (II) is converted by alkali hydroxide into the dieneketonic acid (IV), m.p. 188—

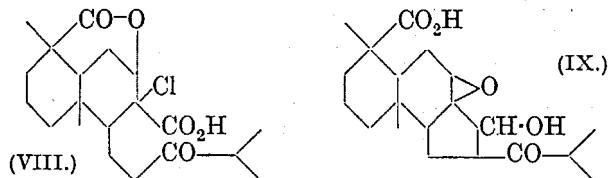


189° [monoxime, m.p. 235° (decomp.)], the absorption spectrum of which indicates the proximity of two conjugated double linkings to CO. Catalytic hydrogenation leads to the corresponding saturated acid (V), analysed as the oxime, m.p. 215—216°, and semicarbazone, m.p. 219—220°. Incomplete hydrogenation yields the H_2 -acid (oxime, m.p. 197—198°). Reduction (Clemmensen) of (V) gives an amorphous acid, characterised as the Me ester, b.p. 150—160°/0.1 mm.), which does not appear to yield aromatic products

when dehydrogenated. The $\alpha\beta$ -unsaturated nature of (III) is proved by the absorption spectrum. Useful



results are not secured by the oxidation of (III) with H_2O_2 and OsO_4 , $\text{Br}-\text{NaOH}$, or O_3 in AcOH . Boiling quinoline transforms (III) into a diketomonocarboxylic acid, $\text{C}_{20}\text{H}_{28}\text{O}_4$, m.p. 176° , which gives an orange-yellow colour with conc. H_2SO_4 or $\text{C}(\text{NO}_2)_4$ and an intense violet-brown colour with FeCl_3 in EtOH . Oxidodehydroxyabiatic acid is oxidised by $\text{Pb}(\text{OAc})_4$ to the cryst. oxidoketoaldehydic acid (VI), m.p. $132-134^\circ$ [dioxime, m.p. $195.5-197^\circ$ (block preheated to 191°)], also obtained by the successive action of $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{Pb}(\text{OAc})_4$ on (I). (VI) is oxidised by $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ to the oxidoketodicarboxylic acid (VII), $\text{C}_{20}\text{H}_{30}\text{O}_6$, m.p. $156-158^\circ$, which does not give cryst. products with $\text{Br}-$



NaOH . HCl transforms (VII) into a (?) chloroketolactonic acid (VIII), m.p. $117-121^\circ$, re-converted into (VII) by $\text{KOH}-\text{EtOH}$. The course of the reaction of MeOH at 100° or $\text{MeOH}-\text{dil. H}_2\text{SO}_4$ at room temp. on (VII) is less obvious; in each case an amorphous product $\text{C}_{20}\text{H}_{30}\text{O}_6$ results which after treatment with NH_2OH gives a substance, $\text{C}_{20}\text{H}_{30}\text{O}_6$, m.p. $184.5-185^\circ$, which cannot at present be formulated. Warm alkali hydroxide transforms (VI) into an isomeric acid, possibly (IX), m.p. $190-192.5^\circ$ (block preheated to 184°) which is monobasic and proved by its absorption spectrum to contain CO and to be devoid of the $\alpha\beta$ -unsaturated CO group. It is converted by $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ into a compound, $\text{C}_{20}\text{H}_{32}\text{O}_7$, m.p. $171-172^\circ$ (block preheated to 168°). All m.p. are corr. H. W.

Diterpenes. XLII. Dehydrogenation of the oxidation products of abiatic acid to 7-hydroxy-1-methylphenanthrene and 6-hydroxy-1:5-dimethylnaphthalene. Synthesis of 7-hydroxy-1:5- and -1:6-dimethylnaphthalene. L. RÚŽICKÁ and L. STERNBACH [with S. KAUFMANN, E. FRIEDLANDER, A. GROB, H. KIRCHENSTEINER, and H. VON SPRECHER] (Helv. Chim. Acta, 1940, 23, 355-363).—Dehydrogenation of dihydroxy- (I), chlorotrihydroxy-, α -tetrahydroxy-, or oxidodihydroxy-abiatic acid by Se or $\text{Pd}-\text{C}$ at $330-340^\circ$ yields 7-hydroxy-1-methylphenanthrene, m.p. $190-191^\circ$ (acetate, m.p. $137-138^\circ$), thus establishing the presence of OH at $\text{C}_{(7)}$ in (I). As subsidiary action the elimination of Pr^3 is observed. Similar dehydrogenation (Se) of keto-trihydroxyabiatic acid gives 1:5:6- $\text{C}_{10}\text{H}_5\text{Me}_2\cdot\text{OH}$, m.p. $162-163^\circ$ (benzoate, m.p. $151-151.5^\circ$), and a dimethylnaphthol, m.p. $99-100^\circ$.

γ -4-Methoxy-2-methylphenylbutyric acid is converted by P_2O_5 in boiling C_6H_6 into 1-keto-7-methoxy-5-methyl-1:2:3:4-tetrahydronaphthalene, b.p. $137^\circ/0.01$ mm., m.p. $57-57.5^\circ$, which with MgMeI affords 7-methoxy-1:5-dimethyl-3:4-dihydronaphthalene, b.p. $150-152^\circ/12$ mm.; this is dehydrogenated by Se at 340° or, preferably, by $\text{Pd}-\text{C}$ at 320° to 7-methoxy-1:5-dimethylnaphthalene, m.p. $86-86.5^\circ$, demethylated (boiling $\text{AcOH}-48\%$ HBr) to 7-hydroxy-1:5-dimethylnaphthalene, m.p. $151.5-152.5^\circ$. 1:2:5- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{MeAc}$ is methylated (Me_2SO_4) to 3-methoxy-4-methylacetophenone, b.p. $127-130^\circ/12$ mm., which is condensed with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn in C_6H_6 to *Et* 3-methoxy- β :4-dimethylcinnamate, b.p. $132-138^\circ/0.6$ mm. This with $\text{Na}-\text{EtOH}-\text{PhOH}$ is reduced to γ -m-methoxy-p-tolylbutan- α -ol, b.p. $100-102^\circ/0.1$ mm., which is transformed successively into the corresponding chloride, b.p. $112-118^\circ/0.6$ mm., iodide, b.p. $124-125^\circ/0.5$ mm., nitrile, b.p. $122-125^\circ/0.2$ mm., and γ -m-methoxy-p-tolylvaleric acid, b.p. $138^\circ/0.2$ mm., m.p. $61.5-62.5^\circ$. This is cyclised by boiling 85% H_2SO_4 to 1-keto-6-methoxy-4:7-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. $107-108^\circ$, which is reduced to 6-methoxy-4:7-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. $130-135^\circ/12$ mm. This is dehydrogenated (Se at 330°) to 6-methoxy-4:7-dimethylnaphthalene, m.p. $70.5-71^\circ$ (picrate, m.p. 143°), demethylated to 7-hydroxy-1:6-dimethylnaphthalene, m.p. $94-95^\circ$. H. W.

Sterols. XCII. Preparation of neotigogenin from sarsasapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 647-648).—Dibromosarsasapogenone and boiling $\text{C}_5\text{H}_5\text{N}$ give a pyridinium salt, m.p. 235° (decomp.), and bromo- $\Delta^{4,5}$ -dehydrosarsasapogenone, m.p. $185-188^\circ$ (decomp.), reduced by $\text{Na}-\text{EtOH}$ to neotigogenin (I), m.p. $198-200^\circ$ (diacetate, m.p. $173-175^\circ$); derived neotigenone, m.p. $207-210^\circ$; cf. A., 1939, II, 517). It follows that the side-chain of (I) is of the sarsasapogenin type, but that the side-chain of tigogenin, chlorogenin, diosgenin, and probably of gitogenin and digitogenin is of the isosarsasapogenin type. R. S. C.

Sterols. XCIII. epi- ψ -Sarsasapogenin, ψ -sarsasapogenone, and ψ -chlorogenin. R. E. MARKER, E. ROHRMANN, and E. M. JONES (J. Amer. Chem. Soc., 1940, 62, 648-649).—epi-Sarsasapogenin [prep. from sarsasapogenone (I) by $\text{Na}-\text{EtOH}$], m.p. $205-207^\circ$, gives an acetate, m.p. $191-193^\circ$, which with Ac_2O at 200° , followed by hot $\text{KOH}-\text{EtOH}$, gives epi- ψ -sarsasapogenin, m.p. $211-213^\circ$, hydrogenated (PtO_2 ; AcOH ; 3 atm.) to a H_2 -derivative, m.p. $135-137^\circ$ (di-p-nitrobenzoate, m.p. $207-209^\circ$), and oxidised by CrO_3-AcOH at room temp. to $\Delta^{16,17}$ -pregnene-3:20-dione (II) and acids. Ac_2O and (I) give ψ -sarsasapogenone, m.p. $165-166^\circ$ [semicarbazone, m.p. $215-216^\circ$ (decomp.)], oxidised (CrO_3) to (II). isoSarsasapogenin acetate and Ac_2O etc. yield ψ -sarsasapogenin, but dihydrosarsasapogenin is unchanged. Chlorogenin with Ac_2O etc. gives ψ -chlorogenin, m.p. $268-270^\circ$, reduced by $\text{H}_2-\text{PtO}_2-\text{EtOH}-\text{AcOH}$ at 3 atm. to a H_2 -derivative, m.p. $269-272^\circ$ (triacetate, m.p. $149-152^\circ$). R. S. C.

Constituents of Helenium species. III. Ester nature of tenulin. E. P. CLARK (J. Amer. Chem.

Soc., 1940, **62**, 597—600; cf. A., 1939, II, 435).—Tenulin (I) contains OH, CO, OAc, and C:C. H_2O_2 in $\text{NaOH-COMe}_2\text{-H}_2\text{O}$ oxidises (I) or isotenulin (II) to *tenulinic acid* (III), $\text{C}_{15}\text{H}_{20}\text{O}_7$, m.p. 343—344° [*Ac* derivative (IV), $+0.5\text{H}_2\text{O}$, m.p. 243° (234—235°) [*Me* ester, m.p. 259—260°, hydrolysed by NaOH to (III)]; *Me* ester, m.p. 208°], but $\text{KMnO}_4\text{-COMe}_2\text{-H}_2\text{O}$ gives (IV). Cone. H_2SO_4 and (II) at 90° give *AcOH* and *deacetylisotenulin*, $\text{C}_{15}\text{H}_{20}\text{O}_4$, m.p. 255°, previously obtained as a by-product in the prep. of (II) and converted into (II) by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$. Dihydroisotenulin and conc. H_2SO_4 similarly give *deacetyldihydroisotenulin*, m.p. 203°, also obtained by hot 10% NaOH . Distillation of (I) gives *pyrotenulin*, $\text{C}_{13}\text{H}_{16}\text{O}_3$, m.p. 235—236°. The *Ac* in (I) or (IV) is very firmly held, being only partly removed by the standard analytical technique.

R. S. C.

Osage orange pigments. III. Fractionation and oxidation. M. L. WOLFROM and A. S. GREGORY (J. Amer. Chem. Soc., 1940, **62**, 651—652; cf. A., 1940, II, 9).—Fractional crystallisation and the mixed m.p. diagram indicate that *Maclura pomifera* contains approx. equal amounts of osajin (*Me*₂ ether, m.p. 118.5°) and pomiferin, oxidised by $\text{H}_2\text{O}_2\text{-KOH-COMe}_2$ to anisic and veratric acids, respectively.

R. S. C.

Cannabidiol and cannabiol, constituents of *Cannabis indica* resin. A. JACOB and A. R. TODD (Nature, 1940, **145**, 350; cf. A., 1939, II, 121).—The resin distilled from Egyptian hashish yields cannabiniol *p*-nitrobenzoate and a second ester (I) of lower m.p. with *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ in $\text{C}_5\text{H}_5\text{N}$. Hydrolysis of (I) gives cannabidiol (II) (Adams *et al.*, A., 1940, II, 80). Acylation of certain fractions of Indian hashish with azobenzene-4-carboxyl chloride gives a cryst. ester, m.p. 117—118°, which, on alkaline hydrolysis, yields a resinous phenol, *cannabiol*.

L. S. T.

Active principles of leguminous fish-poison plants. IV. Isolation of malaccol from *Derris malaccensis*. S. H. HARPER (J.C.S., 1940, 309—314).—From *D. malaccensis* (Kinta type) there has been isolated *l*-malaccol (I), $\text{C}_{20}\text{H}_{16}\text{O}_7$, prisms, m.p. 225°, solidifying to needles, m.p. 244°, $[\alpha]_D^{25} +190^\circ$ in CHCl_3 , $[\alpha]_D +67^\circ$ in C_6H_6 (*oxime*, decomp. 240°) (cf. Meyer *et al.*, A., 1939, II, 176). Racemisation of (I) with NaOAc-EtOH gives *dl*-malaccol (II), m.p. 244° (*oxime*, decomp. 270°), identical with the second form of (I). Hydrogenation ($\text{H}_2\text{-PtO}_2$) of (I) affords *tetrahydromalaccol*, m.p. 222° (*Ac*₃ derivative, m.p. 195°). Both (I) and (II) with NaOAc followed by *i*- EtOH yield an *l*-compound, reduced (Zn-AcOH) to *dehydromalaccol*, m.p. 257°, but by short treatment with NaOAc (I) gives a *substance*, m.p. 257° (*Ac* derivative, m.p. 227°), not identical with the previous compound. The constitution of these substances is discussed and (I) is considered to be 15-hydroxyelliptone.

F. R. S.

Loco weeds. I. Isolation of α - and β -earleine from *Astragalus earlei*. D. C. PEASE and R. C. ELDERFIELD (J. Org. Chem., 1940, **5**, 192—197).—The conc. 70% EtOH -extract of the dried weed is diluted with H_2O , the solution treated with basic Pb acetate, and the resulting solution freed from Pb

(by H_2S) and evaporated at 40°/vac.; extraction of the resin with EtOH at 55°, concn. of the solution after removal of cryst. *d*-pinitol (cf. A., 1940, III, 462), dilution with H_2O , and treatment of the EtOH -freed solution with phosphotungstic acid gives a ppt., which on decomp. with Ba(OH)_2 in aq. COMe_2 and subsequent treatment with picric acid affords a mixture of picrates separated chromatographically (Al_2O_3) into the *tripicrates*, m.p. 184° (some decomp.) and 247°, respectively, of α -earleine (I), $(\text{C}_{16}\text{H}_{37}\text{O}_7\text{N}_3)_x$ [*trihydrobromide*, m.p. 225° (with partial sublimation); *tristypnate*, m.p. 186—188° (decomp.)], and β -earleine (II), $(\text{C}_{16}\text{H}_{37}\text{O}_4\text{N}_3)_x$, m.p. $\sim 187^\circ$ (decomp.) [*tristypnate*, m.p. 209° (decomp.) (sinters $>180^\circ$); *hygroscopic hydrobromide*, m.p. 296° (decomp.) (slow), 304° (decomp.) (rapid heating)]. Formulæ for (I) and (II), which are both very hygroscopic, are derived from analyses of derivatives. Both (I) and (II) are optically inactive, resemble quaternary NH_4 hydroxides, contain CHMe-OH (CHI_3 test; non-reaction with CO reagents) and <1 NH_2 (aliphatic), and do not appear to be toxic to cats.

H. B.

Astaxanthin and its *H* palmitate, m.p. 115°.—See A., 1940, III, 368.

Fungus pigments. IV. Constitution of lactaroviolin. H. WILLSTAEDT (Atti X Congr. Internaz. Chim., 1938, III, 390—397).—Substances lying below lactaroviolin (I) in the chromatographic separation of products from *Lactarius deliciosus*, L. (A., 1935, 495; 1936, 858), are eluted with MeOH and again chromatographed with Al_2O_3 ; between residual (I) and lactarazulene is a zone containing green *verdazulene*, $\text{C}_{15}\text{H}_{16}$ (II), m.p. 90°, believed to be the first green hydrocarbon to be found naturally. (I) combines with reagent *P* of Girard *et al.* (A., 1936, 1397), to a product easily decomposed by dil. acid, and gives a 2:4-dinitrophenylhydrazone, m.p. $<260^\circ$, and a condensation product, m.p. 228°, with 1:3-dimethylbarbituric acid. It also condenses with $\text{CO}_2\text{H-CHMe-CH}_2\text{-CO}_2\text{H}$ and $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$, and thus its *O* is presumably aldehydic.

E. W. W.

Attempted partial asymmetric synthesis. D. DUVEEN and J. KENYON (Bull. Soc. chim., 1940, [v], 7, 165—180).—(—)-2-Furylmethylcarbinol is hydrogenated (Raney Ni in Et_2O at 70—80°/ ~ 10 atm. for 10 hr.) to (+)-2-tetrahydrofurylmethylcarbinol (I), b.p. 68°/17 mm., $\alpha_{\text{D}}^{25} +4.43^\circ$ ($l = 0.5$) (other vals. quoted), in which OH could not be replaced by Cl by means of SOCl_2 or PCl_3 in presence or absence of $\text{C}_5\text{H}_5\text{N}$ or by means of COCl_2 , thus necessitating the abandonment of the attempt to achieve an asymmetric synthesis by the production of $\text{CH}_2\text{-CH}_2\text{O} > \text{CHEt}$. *dl*-2-Tetrahydrofurylmethylcarbinol (II) gives two *H* phthalates, m.p. 70—72° (III) and 62—63° respectively, the former of which appears to be readily resolvable by brucine in COMe_2 . (II) and Ac_2O in $\text{C}_6\text{H}_5\text{N}$ at 100° afford the acetate, b.p. 97°/25 mm. (I), $\alpha_{\text{D}}^{25} +3.31^\circ$, and $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$ at 50° yield (III) and the *H* phthalate, m.p. 67—68°, $[\alpha]_{\text{D}}^{25} +27.51^\circ$ in CHCl_3 .

H. W.

Condensation of furan derivatives. XI. Dienic ketones (aliphatic and furanic), and their

condensation. V. V. TSHELINCEV and G. I. KUZNETSOVA. XII. Polyenic ketones (aliphatic and furanic) and their condensation. V. V. TSHELINCEV and V. I. KUZNETSOV (J. Gen. Chem. Russ., 1939, 9, 1858—1864, 1901—1906).—XI. $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (I), COMe_2 , and aq. NaOH yield chiefly $\text{COMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}$ (II), together with a higher ketone, unidentified, and resinous polymerides of (II). With COMeEt the chief product is *Me* β - $\Delta^{\beta\delta}$ -hexadienyl ketone, b.p. $82^\circ/12$ mm., together with higher ketones and polymerides. Furfuraldehyde (III) and COMe_2 or COMeEt similarly afford α -2-furyl-, b.p. $172^\circ/16$ mm., m.p. 36° , or α -2-furyl- δ -methyl- $\Delta^{\alpha\gamma}$ -hexadien- ϵ -one, b.p. $186^\circ/20$ mm.

XII. 1:3 mixtures of (I) and COMe_2 or COMeEt yield, in addition to the above dienones, $\Delta^{\beta\delta\eta}$ -undecatetraen- ζ -one, b.p. 178 — $182^\circ/16$ mm., and its ϵ -*Me* derivative, b.p. 139 — $143^\circ/8$ mm., respectively. (III) similarly affords α -di-2-furyl- $\Delta^{\alpha\gamma\delta\theta}$ -nonatetraen- ϵ -one. The above dienones and tetraenones readily polymerise with Na , and yield hard films when exposed to the air.

R. T.

Hydrogenation of coumarin and related compounds. P. L. DE BENNEVILLE and R. CONNOR (J. Amer. Chem. Soc., 1940, 62, 283—287).—A pressure drop in hydrogenation of coumarin (I) alone or in EtOH in presence of Cu chromite at 140 — $160^\circ/100$ — 200 atm. (this pressure also below) indicates formation of dihydrocoumarin (II), but at 250° o - $\text{OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{OH}$ (III), b.p. 159 — $161^\circ/5$ mm. [benzoate, m.p. 96.5 — 99.5° (lit. 99 — 100°)], is obtained in 83 — 90% yield. With H_2 -Raney Ni in Et_2O at 100° , (I) gives 90% of (II), which is an intermediate in other hydrogenations. In presence of Raney Ni at 200° in methylcyclohexane (IV) or EtOH up to 50 — 55% of octahydrocoumarin (V), b.p. 144 — $146^\circ/16$ mm. (lit. $145^\circ/10$ mm.), is obtained with 10 — 15% of hexahydrochroman (VI), b.p. 186 — $187^\circ/760$ mm., but on longer hydrogenation at 250° (VI) is the main product (up to 35%); polymerised material is also obtained in these reactions. Hydrogenation of (V) at 250° in presence of Raney Ni in (IV) gives only (VI), but in presence of Cu chromite gives γ -2-hydroxy-1-cyclohexyl- (VII) (50%), b.p. 185 — $186^\circ/35$ mm., and γ -cyclohexyl-propyl alcohol (11%), b.p. 105 — $106^\circ/10$ mm. (α -naphthylurethane, m.p. 82 — 83°) (also obtained from $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{OH}$ by H_2 - Ni in EtOH at 220°). Ni -hydrogenation of (III) in EtOH at 240° gives 40% of (VI) and 37% of (VII). Chroman is best (87%) obtained by treating (III) with PBr_3 in C_6H_6 , first at 5° and then boiling; when hydrogenated (Ni ; 250° ; EtOH), it gives 41% of (VI). Some β -cyclohexylpropionic acid may be formed during Ni -hydrogenation; its Et ester is isolated from reactions in EtOH , but may have been formed by alcoholysis of (II). The mechanism of the hydrogenations of (I) is discussed.

R. S. C.

Vitamin-E. VII. Homologues of α -tocopherol. (Miss) A. JACOB, F. K. SUTCLIFFE, and A. R. TODD (J.C.S., 1940, 327—332).—Benzoylation of toluquinol gives a mixture of toluquinol dibenzoate, m.p. 122° , and 2-hydroxy-5-benzoyloxytoluene, m.p. 113 — 114° , which condenses with phytol (I) in decalin with ZnCl_2 to 6-hydroxy-2:8-dimethyl-2-(4':8':12'-

trimethyltridecyl)chroman, obtained by removal of Bz and chromatographic purification. Similar condensation of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ with (I) is difficult and after hydrolysis the main product is an oil, $\text{C}_{26}\text{H}_{46}\text{O}_3$, which with $\text{Zn}\cdot\text{HBr}\cdot\text{AcOH}$ gives 6-hydroxy-2-methyl-2-(4':8':12'-trimethyltridecyl)chroman, characterised as the acetate, b.p. 190 — 195° (bath temp.)/ 10 — 2 mm. Condensation of 2:1:4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OH})_2$ with (I) affords an oil which apparently consists largely of quinones related to vitamin-K. Earlier observations (cf. A., 1939, II, 274) on the high degree of activity shown by *m*-xylotocopherol have been confirmed (cf. Karrer *et al.*, A., 1939, II, 557). F. R. S.

Flavones derived from hydroxyphloroglucinol. G. BARGELLINI (Atti X Congr. Internaz. Chim., 1938, III, 32).—2:1:3:4:6- $\text{OH}\cdot\text{C}_6\text{HAc}(\text{OMe})_3$, obtained from 1:2:3:5- $\text{C}_6\text{H}_2(\text{OMe})_4$ and $\text{AcCl}\cdot\text{AlCl}_3$, with anisaldehyde gives 2-hydroxy-3:4:6:4'-tetramethoxychalcone (I), which when warmed with dil. HCl in EtOH gives 5:7:8:4'-tetramethoxyflavanone (= Me_4 ether of cartamidin). With SeO_2 in $\text{C}_5\text{H}_{11}\cdot\text{OH}$, (I) gives 5:7:8:4'-tetramethoxyflavone, m.p. 207 — 208° (= Me_4 ether of isoscutellarein). With H_2O_2 in alkaline EtOH , (I) gives 3:5:7:8:4'-pentahydroxyflavone (herbacetin) (cf. Goldsworthy *et al.*, A., 1938, II, 110). E. W. W.

Directed ring-closure in the synthesis of chromans and coumarans from *o*-allylphenols. C. D. HURD and W. A. HOFFMAN (J. Org. Chem., 1940, 5, 212—222).—Several *o*-allylphenyl acetates (A) are converted by HBr in CCl_4 at room temp. (sealed tube) in presence of (i) quinol, *i.e.*, under peroxide-free conditions, into 1-methylcoumarans, and (ii) air or peroxide (ascarirole; Bz_2O_2) into chromans. The reactions are presumably controlled by the direction of addition of HBr to (A), *viz.*, formation of (i) $\text{o-OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHMeBr}$, (ii) $\text{o-OAc}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{Br}$. *o*-Allylphenol (I) itself acts as an anti-oxidant and gives 1-methylcoumaran (II) under all the conditions. Prep. of (A) from the phenols (usually obtained by pyrolysis of the appropriate aryl allyl ethers in CO_2) is usually effected with keten in presence of a little conc. H_2SO_4 (cf. A., 1940, II, 66); *o*-allylphenyl (III), b.p. 110 — $110.5^\circ/11$ mm., 3-allyl-*p*-tolyl (IV), b.p. 126 — $128^\circ/16$ mm., 3-allyl-*o*-tolyl (V), b.p. $127^\circ/14$ mm., 4-bromo-2-allylphenyl (VI), b.p. 154 — $155^\circ/18$ mm., and *o*-crotylphenyl acetate, (VII) b.p. $132^\circ/15$ mm., are thus obtained. *o*- β -Methylallylphenyl acetate (VIII), b.p. 122 — $123^\circ/15$ mm., is prepared using Ac_2O ; keten gives 1:1-dimethylcoumaran also. Prep. of the following compounds is described: (II) or chroman from (III); 1:4-dimethylcoumaran or (mainly) 6-methylchroman from (IV); 1:6-dimethylcoumaran or 8-methylchroman from (V); 4-bromo-1-methylcoumaran or 6-bromochroman from (VI). *o*- γ -Methyl- Δ^{β} -butenylphenyl acetate (IX), b.p. 134 — $135^\circ/12$ mm., (VII), and (VIII) afford 2:2-dimethyl- (X), 2-methyl-, and 3-methyl-chroman, b.p. 102 — $104^\circ/15$ mm., respectively, under all the conditions used. *o*-Crotylphenol, b.p. 117 — $118^\circ/13$ mm., and *o*- γ -methyl- Δ^{β} -butenylphenol (XI), b.p. 120 — $122^\circ/12$ mm., are obtained from NaOPh and $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$, respectively, in C_6H_6 . Ketene-

H₂SO₄ and (XI) give (IX) and (X). A little (II) is formed from (I) and ascaridole at 100°/2 days. H. B.

Dibenzfuran. XVI. Two-stage metallation of 3-bromodibenzfuran. H. GILMAN, W. LANGHAM, and H. B. WILLIS. **XVII. Interaction of bromo-ethers with lithium *n*-butyl.** H. GILMAN, J. SWISLOWSKY, and G. E. BROWN. **XVIII. Isomeric metallation products of phenols and their methyl ethers.** H. GILMAN, H. B. WILLIS, T. H. COOK, F. J. WEBB, and R. N. MEALS (J. Amer. Chem. Soc., 1940, **62**, 346—348, 348—350; 667—669).—XVI. The two-stage nature of metallation of 3-bromodibenzfuran (I) (A., 1939, II, 276) by LiBu^a in Et₂O is confirmed. After boiling for 6 hr. and subsequent action of CO₂, equimol. amounts of reactants give only 3-bromodibenzfuran-1-carboxylic acid, but after 3 hr. give 87.3% of dibenzfuran-3-carboxylic acid [Me ester, m.p. 82—83° (lit. 73—74°)], also obtained (64% yield) from 1 mol. of (I) and 3 mols. of LiBu^a in Et₂O-C₆H₆ after heating at 50° for 6 hr. Similarly, 1 mol. each of *p*-C₆H₄Br·OMe (II) and LiBu^a at 34° give after 20 hr. *p*-OMe·C₆H₄·CO₂H (III) (10%) and 2:5:1-OMe·C₆H₃Br·CO₂H (IV) (10%; 22—28% at 50°); 2 mols. of (II) and 1 mol. of LiBu^a in C₆H₆ at 50° give after 1—10 hr. 47—52% of (IV) or 45% after 20 hr., or in Et₂O at room temp. 52% of (III) after 10 min. Similar results are reported for *p*-C₆H₄I·OMe, *o*-C₆H₄Br·OH, and *o*-C₆H₄Br·NH₂.

XVII. Interchange of Br and Li occurs when LiBu^a reacts with 4-bromo-3-methoxy-, 4-bromo-1-methoxy-, 2-bromo-3-methoxy-, 8-bromo-1-methoxy-, 4-bromo-1:2-dimethoxy-, 4-bromo-1:8-dimethoxy-, 4:5-dibromo-2:6-dimethoxy-, or 2:7-dibromo-3:6-dimethoxy-dibenzfuran, m.p. 260—261°, in boiling C₆H₆ or C₆H₆-Et₂O, the derived carboxylic acids being obtained after treatment with CO₂. The following appear new. *Me* 1-methoxydibenzfuran-4-carboxylate, m.p. 125°. 1:2-Dimethoxydibenzfuran-1-carboxylic acid, m.p. 236° (*Me* ester, m.p. 78°), also obtained from 4-acetyl-1:2-dimethoxydibenzfuran by KMnO₄. 3:6-Dimethoxydibenzfuran-2:7-dicarboxylic acid, m.p. 290° (decomp.) (*Me*₂ ester, m.p. 183—184°).

XVIII. Interaction of 3-hydroxydibenzfuran with LiBu^a in Et₂O-C₆H₆ and subsequent action of CO₂ gives 21.5% of 3-hydroxydibenzfuran-4-carboxylic acid. 1-Hydroxydibenzfuran gives similarly only the 8-carboxylic acid (4.4%). 1-Methoxydibenzfuran gives 1-methoxydibenzfuran-2- (5.3%), m.p. 182—183° (also obtained from the 2-Ac derivative by KMnO₄), and -8-carboxylic acid (9.2%), m.p. 240—242°. *m*-C₆H₄(OH)₂ gives 2:6:1- (31.1%) and some 2:4:1-C₆H₃(OH)₂·CO₂H, but *m*-C₆H₄(OMe)₂ gives only (55%) 2:6:1-C₆H₃(OMe)₂·CO₂H with a little CO[C₆H₃(OMe)₂:2:6]₂.

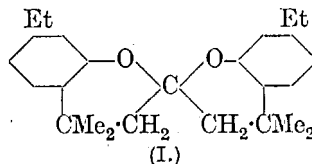
R. S. C.

[Attempted] synthesis of 1:9-benzxanthene. (SIGNA.) E. GHIGI (Atti X Congr. Internaz. Chim., 1938, III, 183—186).—The synthesis of this compound (cf. Kruber, A., 1937, II, 385) is attempted. Xanthone (I) is unaltered by glycerol and 82% H₂SO₄ at 120°. Under similar conditions, xanthhydrol gives (I), as do 9-isoamylxanthhydrol and its perchlorate (cf. Conant *et al.*, A., 1926, 158).

E. W. W.

spiroChromans. J. B. NIEDERL and R. H. NAGEL (J. Amer. Chem. Soc., 1940, **62**, 324—325).—

Condensation of COMe₂ (3 mols.) with *m*-C₆H₄Et·OH (2 mols.) by HCl at 40° gives the *dimeride*, b.p. 200—207°/12 mm., of 3-ethyl-6-isopropenylphenol, converted by a little H₂SO₄ in boiling 95% EtOH into 4:4:4':4'-tetramethyl-7:7'-diethylbis-2:2'-spirochroman (I), dimorphic, m.p. 114° and 146° [(NO₂)₄-derivative,



m.p. 246—248°], obtained in one step by condensing with H₂SO₄ at 25°, and directly from phorone and COMe₂ with HCl at 25°.

R. S. C.

Addition of hydroxy-compounds to acetylenic alcohols. J. F. FRONING and G. F. HENNION (J. Amer. Chem. Soc., 1940, **62**, 653—655).—C₂Na₂ and COMe₂ in liquid NH₃ at -50° give 88% of OH·CMe₂·C≡CH (I). Use of <1 mol. of C₂Na₂ and keeping the mixture for 1 week before hydrolysis gives up to 45% of (OH·CMe₂·C≡C)₂ (II). With MeOH and a little HgO, BF₃·Et₂O, and CCl₃·CO₂H at 45—55°, (I) gives 80% of γγ-dimethoxy-β-methyl-*n*-butan-β-ol (III), b.p. 81°/50 mm., and 4.4% of 2:5-dimethoxy-2:3:3:5:6:6-hexamethyl-5-methylenedioxan (IV), m.p. 107° [also obtained by boiling (III) in MeOH with a trace of acid]. Hot, dil. acid converts (III) or (IV) into COMe·CMe₂·OH. With AcOH and the above catalyst (A), (I) gives COMe·CMe₂·OAc. With MeOH or AcOH and (A), (II) gives 2:2:5:5-tetramethylfuran-3-one (V), probably by way of OH·CMe₂·C(OR)₂·CH₂·CMe₂·OH and the ketal of (V). When heated with a little *p*-C₆H₄Me·SO₃H at 150—180°, (III) gives 1:3:3:4:6:6-hexamethyl-2:5:7-trioxadicyclo[2, 2, 1]heptane (VI), b.p. 165°/750 mm., 81—82°/50 mm. (structure proved by the parachor; cf. Scheibler *et al.*, A., 1922, i, 1108), and 2-methoxy-2:3:3:6:6-pentamethyl-5-methylenedioxan, b.p. 110—112°/50 mm. [reversibly converted into (IV) by acid-MeOH].

R. S. C.

Substitution products of thiopheno-2':3'-3:2-thiophen. F. CHALLENGER and G. M. GIBSON (J.C.S., 1940, 305—309).—Thiopheno-2':3'-3:2-thiophen (I) and PrCl in CS₂ with SnCl₄ give thiophthienyl *Et* ketone, m.p. 92—94° (2:4-dinitrophenylhydrazone, m.p. 251—252°). Mercuration (NaOAc-HgCl₂) of (I) in 70% EtOH affords monochloromercurithiophthen, which with PrCl yields the *Et* ketone, and with AcCl the corresponding *Me* ketone (phenylhydrazone, m.p. 165.5—166°). Oxidation with either I-NaOH or K₃Fe(CN)₆ of the *Et* or *Me* ketone gives thiophthen-carboxylic acid, m.p. 220—220.5° (*p*-nitrobenzyl ester, m.p. 151.5—152°; *anilide*, m.p. 172—174°; *Me* ester, m.p. 96.5—97°), also obtained from (I) and MgEtBr; excess of MgEtBr with (I) yields thiophthendicarboxylic acid (*Me*₂ ester, m.p. 238.5—239.5°). Thiophen and MgEtBr give only thiophen-2-carboxylic acid.

F. R. S.

Catalytic transformations of heterocyclic compounds. XIV. Transformation of oxygen-containing five-membered ring systems into nitrogen- and sulphur-containing rings. J. K. JURIEV, C. M. MINATSCHEV, and K. A. SAMURSKAJA (J. Gen. Chem. Russ., 1939, **9**, 1710—1716).—α-Hydroxy-δ-thiolbutane (I) is very rapidly converted

by treatment with H_2SO_4 into thiophen, also obtained by passing H_2S - δ -chloro-*n*-butanol (II) mixture over Al_2O_3 at 400° . It is concluded that (I) is an intermediate in the production of thiophen from H_2S and tetrahydrofuran (Al_2O_3 catalyst, at 400°). (II) and NH_3 similarly yield pyrrolidine, probably via δ -amino-*n*-butanol.

R. T.

Transformation of tetrabromopyrrole. P. PRATESI (Atti X Congr. Internaz. Chim., 1938, III, 312).— Ag_2O or AgOAc converts tetrabromopyrrole into a blue product, oxidised to dibromomaleimide.

E. W. W.

Molecular association of pyrrole aldehydes. P. PRATESI and V. BERTI (Atti X Congr. Internaz. Chim., 1938, III, 313—317).—2:4-Dimethyl- and 2:4-dimethyl-3-ethyl-pyrrole-5-aldehyde are shown cryoscopically to be dimeric in C_6H_6 , except in very dil. solution. 1-Methylpyrrole-2-aldehyde, which, unlike other pyrrole-aldehydes, is normally aldehydic, is unassociated in C_6H_6 .

E. W. W.

Oximinopyrroles. IX. X. Transformation products of oximinopyrrole. T. AJELLO (Atti X Congr. Internaz. Chim., 1938, III, 7—14, 15—21).—IX. The formation of oximinopyrrole-black, $(\text{C}_4\text{H}_3\text{ON})_x$ (I), from Na oximinopyrrole (II) and CO_2 (cf. Angeli *et al.*, A., 1917, i, 413) is not immediate. A brown product, $(\text{C}_4\text{H}_3\text{ON})_x$ (III), is first obtained; the filtrate, which with further CO_2 gives (I), on extraction with Et_2O yields maleimide mono-oxime (IV), new m.p. 210 — 212° (decomp.) (cf. Cusmano, A., 1918, i, 77) (*Bz* derivative, m.p. 245° ; *Me ether*, m.p. 170°). Resistant to dil. KOH or KOH-EtOH, (IV) with 50% KOH gives NH_3 and a white substance; with mineral acids it forms NH_3 , NH_2OH , and fumaric acid. With H_2SO_4 , (II) gives NO, (III), (IV), and NH_3 , but not (I); when the solution is heated, a black, $(\text{C}_4\text{H}_3\text{O}_2\text{N})_x$ (V), is obtained, with (IV). With H_2SO_4 , (I) gives (IV) and a variable product of composition intermediate between (I) and (V).

X. With $\text{NH}_2\text{OH}\cdot\text{HCl}$ (VI), (II) gives maleimide di-oxime (VIII), m.p. 256° ; with $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HCl}$ (VII), either (II) or (IV) gives a mixture of maleimide semicarbazone (IX), m.p. 230° , and maleimide oxime semicarbazone (X), m.p. 295° . With (VI), both (IX) and (X) give (VIII); with (VII), (VIII) gives (X). These compounds with acid yield fumaric acid. The possibility that (IV) might be 3-oximinomethylisooxazole is considered and rejected.

E. W. W.

Organic catalysts. XVIII. Synthesis of polyenealdehydes as an example of main-valency catalysis. W. LANGENBECK [with O. GÖDDE and L. WESCHKYL (Atti X Congr. Internaz. Chim., 1938, III, 230—238)].—Piperidine (I) is not an ideal catalyst for the formation of polyene-aldehydes, since it takes part in other reactions. $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (II) and (I) give α -dipiperidino- Δ^2 -butene or α -piperidinobutadiene (III). (III) reacts with MeCHO , even at 0° , giving a product which with $\text{AcOH}\cdot\text{Ac}_2\text{O}$ (IV) gives $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$. From (III) and (II), (IV) liberates no octatrienal (V), the only aldehyde formed being *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, presumably by way of $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{C}_5\text{H}_{10}\text{N})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ and 4-piperidino-6-methyl- Δ^1 -cyclohexen-1-al. Mechanisms, including that of the formation of (V) from (I) and

(II), are discussed. For the formation of non-cyclic products only, a catalyst is needed that is lost from the intermediate faster than this can cyclise.

E. W. W.

Reactivity of bromine atoms in brominated pyridines. Formation of 6-bromo-2-hydroxypyridine by acid hydrolysis of 2:6-dibromopyridine. J. B. WIBAUT, P. W. HAAYMAN, and J. VAN DIJK (Rec. trav. chim., 1940, 59, 202—206).—2:6-Dibromopyridine and 70% H_2SO_4 , 60% AcOH or HCO_2H , or (best) 80% H_3PO_4 , at 160° , give 6-bromo-2-hydroxypyridine; the use of aq. $\text{NaOH}\cdot\text{C}_5\text{H}_5\text{N}$ causes decomp. (cf. A., 1936, 481). The results of Seide *et al.* (A., 1936, 1264) on aminopyridines are confirmed.

A. T. P.

Sulphanilamide derivatives. V. Constitution and properties of 2-sulphanilamidopyridine. M. L. CROSSLEY, E. H. NORTHEY, and M. E. HULTQUIST (J. Amer. Chem. Soc., 1940, 62, 372—374; cf. A., 1939, II, 542).—Conversion of 2-aminopyridine (I), m.p. 57 — 58° (f.p. $57\cdot9^\circ$), by *p*- $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$, m.p. $148\cdot5$ — $149\cdot5^\circ$, in anhyd. dioxan at 95° into 2-*N*⁴-acetylsulphanilamidopyridine, m.p. $226\cdot6$ — $228\cdot1^\circ$ (tube; softens at $225\cdot2^\circ$), $230\cdot5^\circ$ (block; immediate), 229° (block; heating from room temp.), and thence by boiling aq. NaOH into 2-sulphanilamidopyridine (II), m.p. $190\cdot9$ — $191\cdot5^\circ$ (tube; shrinks at $190\cdot4^\circ$), $192\cdot8^\circ$ (block), is described. The conventional structure of (II) is indicated by hydrolysis by boiling 36% HCl (not 50% NaOH) to (I) and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ and by the p_{H} (10—11) of its Na salt in H_2O . Oxidation and anaerobic decomp. occur when (II) is melted.

R. S. C.

Pyridines of sulphanilamide type.—See B., 1940, 244.

Nitrosoacylarylamines. IV. Action of some nitrosoacylarylamines on pyridine. J. W. HAWORTH, I. M. HEILBRON, and D. H. HEY (J.C.S., 1940, 372—374).— $\text{NPhAc}\cdot\text{NO}$ and $\text{C}_5\text{H}_5\text{N}$ at room temp., followed by fractionation of the respective picrates, give a mixture of 2-, 3-, and 4-phenylpyridine in ~60% yield (theoretical aspects are discussed). *p*- $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{NO}$ and $\text{C}_5\text{H}_5\text{N}$ at 80° give a mixture of *p*-benzamidophenylpyridines, m.p. 204 — 214° . 2-Acetamidopyridine (I) or its methiodide or methosulphate could not be nitrosated; (I) and nitrous fumes in $\text{AcOH}\cdot\text{Ac}_2\text{O}$ give the pyridinium nitrate. *p*- $\text{C}_6\text{H}_4(\text{NAc}\cdot\text{NO})_2$ and $\text{C}_5\text{H}_5\text{N}$ at 40 — 50° give *p*- $\text{C}_6\text{H}_4(\text{NHAc})_2$ and a mixture, m.p. 123 — 126° , of 2- and 4-*p*-acetamidophenylpyridines, hydrolysed by HCl to 2-, m.p. 228 — 230° , and 4'-*p*-aminophenylpyridine, m.p. 97 — 98° .

A. T. P.

Selenium oxychloro-compounds of pyridine, pyridinium chloride, and related substances.—See A., 1940, I, 229.

Arylpyridines. I. Phenylpyridines and nitrophenylpyridines. J. W. HAWORTH, I. M. HEILBRON, and D. H. HEY. II. Some substituted phenylpyridines. E. C. BUTTERWORTH, I. M. HEILBRON, and D. H. HEY. III. Anisyl- and nitroanisyl-pyridines. J. W. HAWORTH, I. M. HEILBRON, and D. H. HEY (J.C.S., 1939, 349—355, 355—358, 358—361).—I. The slow addition of an aq.

solution of a diazonium salt to an excess of C_5H_5N (temp. $\sim 20^\circ$ to 70° according to amine used) gives a mixture of arylpyridines (20–80% yield), which can be separated by appropriate treatment. PhN_2Cl at 30° affords a mixture of 2-, 3-, and 4-phenylpyridines (40% yield) separated through the picrates, the 2-isomeride predominating. $p\text{-NO}_2\cdot C_6H_4\cdot N_2Cl$ at 40° yields a mixture (70% yield) of 2-, 3- (*picrate*, m.p. 220°), and 4-nitrophenylpyridine (*picrate*, m.p. 228–229°) and 2:6-di-*p*-nitrophenylpyridine, m.p. 293°. $m\text{-NO}_2\cdot C_6H_4\cdot N_2Cl$ at 40° gives a mixture of 2- (*picrate*, m.p. 157°), 3-, m.p. 101–102° (*picrate*, m.p. 200–201°), and 4-m-nitrophenylpyridine (*picrate*, m.p. 250°). Similarly $o\text{-NO}_2\cdot C_6H_4\cdot N_2Cl$ at 40° affords 2- (*picrate*, m.p. 151–152°), 3- (*picrate*, m.p. 182–183°), and 4-o-nitrophenylpyridine (*picrate*, m.p. 206–207°). The constitution of the compounds has been established by reduction of NO_2 and elimination of NH_2 to known compounds. Suggestions are put forward with regard to the reaction mechanism.

II. In this series only two isomerides have been isolated, the major product being the 2-derivative; the second constituent is regarded as the 4-isomeride. From the appropriate diazonium chloride the following have been isolated: 4-, m.p. 70–71° (*picrate*, m.p. 225–227°), and 2-*p*-chlorophenylpyridine, m.p. 52–53° (*picrate*, m.p. 169–170°; also obtained from α -4-aminophenylpyridine); 4-, m.p. 129–131° (*picrate*, m.p. 213–214°), and 2-*p*-bromophenylpyridine, m.p. 62° (*picrate*, m.p. 168°; also obtained synthetically); 2- and 4-*p*-phenetylpyridine, m.p. 100–101° (*picrate*, m.p. 199–200°); and 2-*p*-carboxyphenylpyridine, m.p. 232° (*Me* ester, m.p. 90°; also obtained by hydrolysis of 2-*p*-cyanophenylpyridine, m.p. 97–98°: presence of 4-compound shown by decarboxylation to 4-phenylpyridine). 2-*p*-Iodophenylpyridine, m.p. 85–86°, is described.

III. $o\text{-OMe}\cdot C_6H_4\cdot N_2Cl$ at $70\text{--}80^\circ$ gives 2- (I) (*picrate*, m.p. 155–156°), 3- (*picrate*, m.p. 182°; synthesised from 4-o-aminophenylpyridine), and 4-o-anisylpyridine (*picrate*, m.p. 205°). (I) is oxidised ($KMnO_4$) to picolinic acid and nitrated (fuming HNO_3) to 2-5'-nitro-2'-methoxyphenylpyridine, m.p. 126–127°, also prepared from diazotised 4-nitro-o-anisidine and C_5H_5N . Diazotised 5-nitro-o-anisidine and C_5H_5N gives a mixture of 2-, m.p. 132–133° (*picrate*, m.p. 163–164°), and 4-4'-nitro-2'-methoxyphenylpyridine, m.p. 115° (*picrate*, m.p. 215–216°). Similarly diazotised *p*-anisidine affords 2-, m.p. 49–50° (*picrate*, m.p. 191–192°; nitrated to the -3'- NO_2 -derivative, m.p. 85–86°), and 4-4'-methoxyphenylpyridine, m.p. 95° (*picrate*, m.p. 205–206°). *m*-Anisidine forms 2- (*picrate*, m.p. 154–155°) and 4-3'-methoxyphenylpyridine (*picrate*, m.p. 203–204°).

F. R. S.

Structural problems in the indole group. IV. Alternative method for determining the structure of nitro-compounds. S. G. P. PLANT and W. D. WHITAKER (J.C.S., 1940, 283–286).—4(or 6)-Nitro-8-acetyldihydropentindole (A., 1936, 1124) in AcOH with HNO_3 gives 6:10-dinitro-9-hydroxy-8-acetyltetrahydropentindole, m.p. 215° (decomp.), which with KOH affords γ -4-nitro-2-acetamidobenzoylbutyric acid, m.p. 165°, oxidised ($KMnO_4$) to 4:2:1- $NO_2\cdot C_6H_3(NHAc)\cdot CO_2H$ (I); the original compound

is thus the 6-derivative. 5-Chloro-4(or 6)-nitro-8-acetyldihydropentindole (A., 1931, 1165) similarly yields 5-chloro-6:10-dinitro-9-hydroxy-8-acetyltetrahydropentindole, m.p. 198° (decomp.), degraded (KOH) to γ -5-chloro-4-nitro-2-acetamidobenzoylbutyric acid, m.p. 133°, which is oxidised ($KMnO_4$) to 5-chloro-4-nitro-2-acetamidobenzoic acid, m.p. 250° (decomp.), also obtained by oxidation of the corresponding toluene; the 4(or 6) compound is thus the 6-derivative. *Me* 5-chloro-4-nitroanthranilate, m.p. 140°, is prepared from the corresponding acid and HCl-MeOH. The 2-chloro-5-nitrophenylhydrazone of COMeEt with AcOH-HCl gives 7-chloro-4-nitro-2:3-dimethylindole, m.p. 218°, reduced (Sn-HCl) to 4-amino-2:3-dimethylindole, m.p. 163°; the reduction product of 4(or 6)-nitro-2:3-dimethylindole (A., 1933, 1057) was a gum. Nitration of 4(or 6)-nitro-1-acetyl-2:3-dimethylindole affords 3:6-dinitro-2-hydroxy-1-acetyl-2:3-dimethyl-2:3-dihydroindole, m.p. 198° (decomp.), degraded and oxidised to (I), indicating identity of the original substance with the 6-derivative. 1-Acetyl-2:3-dimethylindole gives on nitration 2:3-dihydroxy-1-acetyl-2:3-dimethyl-2:3-dihydroindole, m.p. 132–134°, in addition to the 6- NO_2 -derivative previously isolated. cyclopentanone-2-chloro-5-nitrophenylhydrazone, m.p. 101°, with H_2SO_4 yields 7-chloro-4-nitrodihydropentindole, m.p. 251°.

F. R. S.

Gramicidin, $C_{74}H_{106}O_{14}N_{14}$, m.p. 228–230°, $[\alpha]_D^{25} +5^\circ$, gramicin acid, $C_{44}H_{63}O_{11}N_9$, m.p. 232–234°, $[\alpha]_D^{25} -115^\circ$, and gramicidin acid, m.p. 230°, $[\alpha]_D^{25} -100^\circ$ (all in 95% EtOH).—See A., 1940, III, 352.

Reaction of tetrahydroquinoline with α -oxides. V. I. KOROLEVA (J. Gen. Chem. Russ., 1939, 9, 2200–2202).—1:2:3:4-Tetrahydroquinoline and $(CH_2)_2O$ (6–8 hr. at $60\text{--}70^\circ$) or propylene oxide (12 hr. at 70°) yield N- β -hydroxyethyl-, b.p. 292–293° (*picrate*, m.p. 75°) or N- β -hydroxypropyl-1:2:3:4-tetrahydroquinoline, b.p. 165–170°/10 mm. (*picrate*, m.p. 95°).

R. T.

3-Methyl-3:4-di- and -1:2:3:4-tetrahydroisoquinolines. W. S. IDE and J. S. BUCK (J. Amer. Chem. Soc., 1940, 62, 425–428).—3:4-Methylenedioxy-, m.p. 200°, and 3:4-dimethoxy- α -methylcinamic acids *cis*-, m.p. 144°, and *trans*-form, m.p. 232°, are obtained by condensing ArCHO and EtCO₂Et by "at." Na and hydrolysing the product or by treating ArCHO with CHMeBr·CO₂Et and Zn in C_6H_6 and dehydrating (POCl₃) and hydrolysing the product. β -3:4-Dimethoxy-, m.p. 109°, and β -3:4-methylenedioxy-phenylisobutyramide (prep. from the NH_4 salt at 220° or from the acid chloride), m.p. 122°, with NaOCl give $CH_2Ar\cdot CHMe\cdot NH_2$, Ar = 3:4-(OMe)₂C₆H₃, b.p. 154°/9 mm., or 3:4-(CH₂O)₂C₆H₃, b.p. 143–145°/11 mm. (hydrochloride, new m.p. 183–185°). The following are obtained by conventional reactions starting with Bischler-Napieralski condensation of $CH_2Ar\cdot CHMe\cdot NH\cdot CHO$. 6:7-Dimethoxy-, m.p. 189°, -methylenedioxy-, m.p. 198°, and -dihydroxy-, m.p. 297°, -3-methyl-3:4-dihydroisoquinoline hydrochloride. 6:7-Dimethoxy-, new m.p. 245°, -methylenedioxy-, m.p. 238°, and -dihydroxy-, m.p. 270°, -3-methyl-1:2:3:4-tetrahydroisoquinoline hydrochloride. 6:7-

Dimethoxy-, m.p. 125—128° (corresponding *iodide*, m.p. 156°), *-methylenedioxy*-, m.p. 212° (corresponding *iodide*, m.p. 213°), and *-dihydroxy*-, m.p. 199°, -2 : 3-dimethyl-3 : 4-dihydroisoquinolinium chloride. 6 : 7-*Dimethoxy*-, m.p. 100° (*hydrochloride*, m.p. 232°), *-methylenedioxy*-, new m.p. 88° (*hydrochloride*, new m.p. 228—229°), and *-dihydroxy*- (*hydrochloride*, m.p. 266°) -2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline. 6 : 7-*Dimethoxy*-, m.p. 239° (corresponding *iodide*, m.p. 232°), *-methylenedioxy*-, m.p. 248—250° (corresponding *iodide*, m.p. 242°), and *-dihydroxy*-, m.p. 258°, -2 : 2 : 3-trimethyl-1 : 2 : 3 : 4-tetrahydroisoquinolinium chloride. M.p. are corr. R. S. C.

Organolithium compounds of pyridine and quinoline. H. GILMAN and S. M. SPATZ (J. Amer. Chem. Soc., 1940, 62, 446).—3-Bromoquinoline reacts readily with LiBu^a in Et_2O at -35° ; the product, with CO_2 , gives 52% of quinoline-3-carboxylic acid. 3-Bromopyridine similarly gives 70% of nicotinic acid. $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ gives 31% of $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. R. S. C.

Reaction of elimination of hydrogen bromide from aliphatic dibromides. II. A. M. BERKENHEIM and T. F. DANKOVA (J. Gen. Chem. Russ., 1939, 9, 1801—1807).— $\alpha\delta$ -Dibromopentane (I) and quinoline at 170—175° give piperylene in 4—5% yield; an additive product is also formed, and this with NaOH gives $\alpha\delta$ -di-(2-keto-N-quinolino)pentane, m.p. 130—136° (decomp.). (I) and NPhMe_2 react at 175—180° as follows: (I) $\rightarrow \text{NPhMe}_2 \rightarrow \text{C}_5\text{H}_9\text{Br} + \text{NPhMe}_2\cdot\text{HBr}$ (II); (II) $\rightarrow \text{NHPhMe} + \text{MeBr}$; $\text{NHPhMe}\cdot\text{HBr} \rightarrow \text{NH}_2\text{Ph} + \text{MeBr}$; $\text{NH}_2\text{Ph} + \text{(I)} \rightarrow 1\text{-phenyl-2-methylpyrrolidine}$. (I) and KOH in EtOH give piperylene in 9—10% yield, but the chief product is the unsaturated ether, $\text{C}_5\text{H}_9\cdot\text{OEt}$, together with the saturated ether $\alpha\delta\text{-C}_5\text{H}_{10}(\text{OEt})_2$. With KOH-EtOH the monobromide $\text{C}_5\text{H}_9\text{Br}$ gives piperylene in 60%, and $\text{C}_5\text{H}_9\cdot\text{OEt}$ in 17%, yield. R. T.

Inner complex salts of 8-hydroxyquinoline-5-sulphonic acid.—See A., 1940, I, 230.

Anti-malarials of the 8-aminoalkylamino-6-methoxyquinoline series. A. A. BEER (J. Gen. Chem. Russ., 1939, 9, 2158—2161).—8-Amino-6-methoxyquinoline, condensed with *N*- ω -halogenoalkylphthalimide, yields 8-phthalimidomethyl- (*hydrobromide*, m.p. 207—209°), 8- β -phthalimidoethyl-, 8- γ -phthalimidopropyl-, m.p. 102—103° (*hydrochloride*, m.p. 200—201°), 8- δ -phthalimidobutyl-, and 8- ϵ -phthalimidoamyl-amino-6-methoxyquinoline, m.p. 115—116° (*hydriodide*, m.p. 156—157.5°). These products, boiled with N_2H_4 in EtOH, yield 8-amino-methyl- (I), m.p. 279—280° (*dihydrochloride*, $+\text{H}_2\text{O}$, m.p. 179—180°), 8- β -aminoethyl-, 8- γ -aminopropyl- (II) (*dihydrochloride*, m.p. 251—252°, $+\text{H}_2\text{O}$, m.p. 235—238°), 8- δ -aminobutyl- (*dihydrochloride*, $+\text{H}_2\text{O}$, m.p. 182—183°), and 8- ϵ -aminoamyl-amino-6-methoxyquinoline (*dihydrochloride*, $+\text{H}_2\text{O}$, m.p. 156—157°). (I) has no anti-malarial action; of the remaining substances (II) is the most active. R. T.

Quinoline compounds as basic substances for preparation of medicinal products. VIII. **Anæsthetics of the cinchonamide series.** O. J. MAGIDSON, M. V. FEDOTOVA, and V. V. ZVEREV (J.

Gen. Chem. Russ., 1939, 9, 2097—2103).—2-Chlorocinchonyl chloride and $\text{NH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{NEt}_2$ in Et_2O yield the 8-diethylamino- α -methylbutylamide of 2-chlorocinchonic acid, m.p. 91—93°, which when heated (3 hr. at the b.p.) with various alkoxides (NaOR in ROH) yields the corresponding 2-OR-derivatives [$\text{R} = \text{Me}$, b.p. 220—224°/1.5—2 mm., T.I. = 1.25; $\text{R} = \text{Et}$, b.p. 218—222°/2—2.5 mm., T.I. = 0.75; $\text{R} = \text{Pr}^B$, b.p. 220°/1—1.5 mm., T.I. = 3; $\text{R} = \text{Bu}^a$, b.p. 222—228°/1.5—2 mm., T.I. = 1.2; $\text{R} = n\text{-octyl}$, m.p. 80—81°, T.I. = 3 (T.I. = therapeutic index = $100 \times \text{min. lethal/min. effective dose}$)]. The 8-diethylaminobutylamide of 2-chlorocinchonic acid, m.p. 45—48°, yields similarly the following 2-OR-compounds: $\text{R} = \text{Et}$, m.p. 62—63°, T.I. = 0.3; $\text{R} = \text{Bu}^a$ (Percaine), T.I. = 12.5. The γ -diethyl-amino- β -hydroxypropylamide of 2-chlorocinchonic acid, an oil, similarly gives the following 2-OR-compounds: $\text{R} = \text{Me}$, m.p. 75—76°, T.I. = 14; $\text{R} = \text{Et}$, m.p. 85—86°, T.I. = 3; $\text{R} = \text{Bu}^a$, m.p. 53—54°, T.I. = 6. R. T.

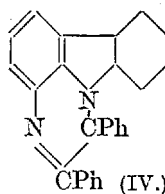
Alkaloid-like compounds from brasilin and hæmatoxylin. P. PFEIFFER, J. BREITBACH, and W. SCHOLL (J. pr. Chem., 1940, [ii], 154, 157—208).—Trimethylbrasilinol and $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{EtOH}$, or the corresponding oximes (cf. A., 1933, 832), are converted by NaOH into 6 : 7-dimethoxy-1-(2'-hydroxy-4'-methoxyphenyl)-3-methylisoquinoline 2-oxide, m.p. 243° [*hydrochloride*, m.p. $\sim 131^\circ$ (decomp.)]; *Bz* derivative, m.p. 176°; (2'-)*Me* ether (*hydrochloride*, m.p. 110—115°; *picrate*, m.p. 180—185°], reduced by SO_2 or $\text{Zn}\cdot\text{AcOH}$ to the corresponding -isoquinoline, m.p. 188—189° [*picrate*, m.p. 224—225°; *methiodide* ($+1.33\text{H}_2\text{O}$), m.p. 227—228°; (2'-)*Me* ether, m.p. 110° (*picrate*, m.p. 212—215°, with previous softening; *methiodide*, m.p. 160°)]. Tetramethylhæmatoxylinol affords the *oxime*, m.p. 223° (previous sintering), converted by NaOH-EtOH at 100° (bath) into 6 : 7-dimethoxy-1-(2'-hydroxy-3' : 4'-dimethoxyphenyl)-3-methylisoquinoline 2-oxide (I), m.p. 220° (stable) (a form, m.p. 191—192°, is converted, by keeping in closed vessels, into the stable form) [$\text{Me}_2\text{SO}_4\cdot\text{C}_6\text{H}_6$, then aq. KI, gives the *methiodide*, m.p. 206—208° (sinters at 170°, decomp. 210°); *picrate*, m.p. 216—217°], reduced in AcOH by Zn or SO_2 to the corresponding -isoquinoline (II), m.p. 174° [*hydrochloride*, m.p. 230—250° (decomp.)]; *picrate*, m.p. 210° (previous sintering); *Ac* derivative, m.p. $\sim 86\text{--}88^\circ$ (*picrate*, m.p. 202—203°; *methiodide*, $+\text{H}_2\text{O}$, m.p. 118° (sinters at 115°; decomp. 120—123°)]. (II)- $\text{Me}_2\text{SO}_4\cdot\text{C}_6\text{H}_6$ give the *methosulphate*, m.p. 168—170°, converted by aq. KI into the *methiodide* (III), m.p. 230—231°, also prepared from (II)- $\text{MeI}\cdot\text{CHCl}_3$. (II)- $\text{Me}_2\text{SO}_4\cdot\text{aq. NaOH}$ give the *Me* ether, 6 : 7-dimethoxy-1-(2' : 3' : 4'-trimethoxyphenyl)-3-methylisoquinoline (IV), m.p. 129—130° [*picrate*, m.p. 185—186° (sinters from 165°)]; its *methiodide*, m.p. 227—228°, is obtained, together with (IV), from (II)- $\text{MeI}\cdot\text{aq. NaOH}\cdot\text{MeOH}$, or from (I)- $\text{MeI}\cdot\text{NaOH}$. (II) and $\text{Na}\cdot\text{EtOH}$ afford 6 : 7-dimethoxy-1-(2'-hydroxy-3' : 4'-dimethoxyphenyl)-3-methyltetrahydroisoquinoline (V), m.p. 181—184° [*picrate*, $+\text{H}_2\text{O}$, m.p. 175—178°, decomp. 195—196° (2 forms)]. (III)- $\text{AgCl}\cdot\text{aq. MeOH}$ give the *methochloride*, converted by $\text{Sn}\cdot\text{HCl}$ into the *N-Me* derivative [*picrate*, m.p. 190° (previous sintering)] of

(V). (II) and aq. KMnO_4 -NaOH give metahemipinic acid, m.p. 179 — 180° (*N*-ethylimide, m.p. 228°). (II) and HNO_3 (*d* 1.25) give 6:7-dimethoxy-3-methylisoquinoline-1-carboxylic acid [*picrate*, +MeOH or + H_2O , m.p. 240° (decomp.) (sinters at 230°); Me ester (*picrate*, m.p. 212° , sinters at 205° , decomp. at 216°)]. β -Acetamido- α -3:4-dimethoxyphenylpropan- α -ol (cf. Buckner *et al.*, A., 1935, 972) and $2\text{N}\cdot\text{H}_2\text{SO}_4$ at 100° (bath) give the β - NH_2 -compound (VI), new m.p. 128 — 129° , which with dimethyl- β -resorcylyl chloride, m.p. 54 — 56° (*amide*, m.p. 132° ; *anilide*, m.p. 141°), affords β -(2:4-dimethoxybenzamido)- α -(3:4-dimethoxyphenyl)propan- α -ol, converted by POCl_3 -PhMe into 7:8-dimethoxy-1-(2':4'-dimethoxyphenyl)-3-methylisoquinoline, m.p. 144 — 145° (cf. isomeride, m.p. 110° , above) (chromatographic analysis) [*picrate*, m.p. 232 — 235° ; Me_2SO_4 in C_6H_6 gives the *methosulphate*, m.p. 239° , converted by KI into the *methiodide*, m.p. 217 — 219° (decomp.); Na-EtOH give the H_4 -derivative (*picrate*, m.p. 203 — 205° , sinters at 190°)]. 4:2:1- $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$ and $\text{NHMe}_2\cdot\text{C}_6\text{H}_6\cdot\text{Et}_2\text{O}\cdot\text{ClCO}_2\text{Et}$ at room temp. give 2-carbethoxyhydroxy-4-methoxybenzoic acid, m.p. 111° (*anilide*, m.p. 215°); its chloride and (VI) give β -(4-methoxy-2-carbethoxyhydroxybenzamido)- α -(3:4-dimethoxyphenyl)propan- α -ol, converted by POCl_3 -PhMe into 7:8-dimethoxy-1-(2'-hydroxy-4'-methoxyphenyl)-3-methylisoquinoline [*picrate*, sinters at 265° , decomp. 272 — 275° (cf. isomeride, m.p. 224 — 225° , above)]. 2:3:4:1- $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{COCl}$ and (VI) give β -(2:3:4-trimethoxybenzamido)- α -(3:4-dimethoxyphenyl)propan- α -ol, m.p. 127 — 128° , converted into 7:8-dimethoxy-1-(2':3':4'-trimethoxyphenyl)-3-methylisoquinoline, m.p. 110 — 112° (cf. above isomeride) [*picrate*, m.p. 183 — 184° ; *methosulphate*, m.p. 225 — 227° ; *methiodide*, m.p. 226 — 227° (decomp.)].

A. T. P.

Indoles. VII. Stereochemistry of tervalent nitrogen. F. LIONS and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1939, 73, 125—149; cf. A., 1939, II, 449).—Attempts are described to prepare compounds in the mol. of which a N atom is common to two ring structures which are at the same time plane and co-planar. Hexahydrocarbazole (I) and ClCO_2Et at 100° in absence of moisture give 9-carbethoxyhexahydrocarbazole, b.p. 200 — $202^\circ/20$ mm. Contrary to Manjunath (A., 1927, 978), 9-nitroso-hexahydrocarbazole could not be obtained cryst. 8:9-1':2'-cyclohexylenetetrahydrocarbazole has m.p. 77° [Manjunath (*loc. cit.*) records m.p. 83°]. $\delta\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}_2$ (prep. described) and cyclohexanone (I) in warm EtOH give the very unstable cyclohexanone-o-tolylhydrazone, m.p. 59 — 60° , readily cyclised in boiling glacial AcOH to 8-methyl-1:2:3:4-tetrahydrocarbazole, m.p. 98° [*picrate*, m.p. 136° (decomp.)]. 8-Methyl-1:2:3:4:10:11-hexahydrocarbazole, b.p. $177^\circ/28$ mm. [*picrate*, m.p. 159 — 160° (decomp.)], is converted by NaNO_2 and AcOH into 9-nitroso-8-methylhexahydrocarbazole, m.p. 68° , which with Zn dust and AcOH containing (II) gives 8-methyltetrahydrocarbazole. Reduction of nitrosoindoline with Zn dust and glacial AcOH containing (II) affords 8:9-dimethylene-1:2:3:4-tetrahydrocarbazole, m.p. 154° [*picrate*, m.p. 141° (decomp.)], whereas in presence of AcCO_2H or AcCO_2Et the sole

isolable product is a small amount of the initial material. (I) is transformed by $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ at 100° into *Et* hexahydrocarbazole-9-acetate, b.p. 204 — $206^\circ/20$ mm., which is not cyclised by conc. H_2SO_4 at room temp. or at 100° , by being preheated at 100° and dropped into liquid paraffin at 280° , or by being heated at 300° . It is hydrolysed by boiling KOH-EtOH to 9-methylhexahydrocarbazole (III), b.p. $163^\circ/26$ mm. [*picrate*, m.p. 146 — 147° (decomp.); *methiodide*, m.p. 195°]. (I) and $\text{CHBr}(\text{CO}_2\text{Et})_2$ at 100° yield *Et*₂ hexahydrocarbazole-9-malonate, b.p. 190 — $193^\circ/2$ mm., which does not appear to be cyclised at 280° ; it is converted by KOH-EtOH into (III) and the unstable hexahydrocarbazole-9-malonic acid, m.p. 93 — 95° . Glyoxal H sulphite and (I) in boiling aq. EtOH slowly yield 9-hexahydrocarbazolylacetyl-9'-hexahydrocarbazole, m.p. 221 — 222° . 9-Phenacylhexahydrocarbazole, m.p. 112° , from (I) and CH_3BzBr in boiling EtOH, is unchanged by conc. H_2SO_4 at room temp., gives tarry products and unchanged material with conc. H_2SO_4 at 100° , yields tar and unchanged material when boiled with cumene containing ZnCl_2 , and is unaffected by P_2O_5 in boiling xylene; at 180° it is converted into tar. Phenacylaniline and (I) at 180 — 190° afford 2-phenylindole, m.p. 186° (*picrate*, m.p. 139°), obtained similarly in the absence of (I). 8-Nitrotetrahydrocarbazole is reduced by Sn, conc. HCl, and EtOH at 100° to 8-amino-1:2:3:4:10:11-hexahydrocarbazole, m.p. 159 — 160° (decomp.) [*picrate*, m.p. 172 — 173° (decomp.)], which is reasonably stable when solid but is rapidly oxidised in solution. It is converted by boiling abs. HCO_2H or Ac_2O into the *formyl*, m.p. 192° , and *Ac*, m.p. 201° , derivatives, no basic compounds being found in the mother-liquors.



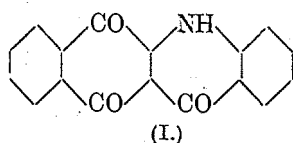
Even under mild conditions it forms tarry products with benzoin with which in glacial AcOH it yields the *substance* (IV), m.p. 159° . (I) is slowly transformed by boiling $\text{Cl}[\text{CH}_2]_3\text{Br}$ into 8:9-trimethylenehexahydrocarbazole, b.p. 149 — $151^\circ/2$ mm. [*picrate*, m.p. 144° (decomp.); *styphnate*, m.p. 160° (decomp.); *methiodide*, m.p. 156°]. Boiling $\text{CH}_3(\text{CO}_2\text{Et})_2$ and (I) give 9-carbethoxyacetylhexahydrocarbazole, m.p. 78° , which is sol. in dil. NaOH but does not give a colour with FeCl_3 . At 270° it evolves EtOAc and gives (I) and *substances*, (?) $\text{C}_{13}\text{H}_{15}\text{ON}$, m.p. 168° and 186° respectively. At 200° (I) and $\text{CH}_3(\text{CO}_2\text{Et})_2$ yield *malonyldi*hexahydrocarbazole, m.p. 185° . 6-Methyl-1:2:3:4-tetrahydrocarbazole, m.p. 144° (*picrate*, m.p. 147°) (improved prep. from cyclohexanone-*p*-tolylhydrazone), is reduced by Sn and conc. HCl in EtOH at 100° to 6-methyl-1:2:3:4:10:11-hexahydrocarbazole, b.p. $179^\circ/26$ mm. [*picrate*, m.p. 165° ; 9-*Ac* derivative (V), m.p. 95°], which, contrary to Manjunath (*loc. cit.*), could not be caused to solidify. Cautious addition of KNO_3 to an ice-cold solution of (V) in conc. H_2SO_4 gives (probably) 8-nitro- (VI), m.p. 159° , whereas addition of (V) to fuming HNO_3 (*d* 1.5) at 0 — 5° (leads to (probably) 5:8-dinitro-, m.p. 200° , -9-acetyl-6-methylhexahydrocarbazole. (VI) is hydrolysed to 8-nitro-6-methylhexahydrocarbazole, b.p. 210 — $212^\circ/2$ mm. [*picrate*, m.p. 160 — 161° (decomp.)]. Pyrolysis of 9-nitroso-, 9-nitroso-8-methyl-, and 9-nitroso-6-methyl-

hexahydrocarbazole gives mixtures of the corresponding N-free hexa- and tetra-hydrocarbazoles.

H. W.

Heterocyclic local anaesthetics. Carbazole, dibenzfuran, and dibenzthiophen derivatives. R. R. BURTNER and G. LEHMANN (J. Amer. Chem. Soc., 1940, **62**, 527—532).—Carbazole-3-carboxylic acid (I), Bu_2SO_4 , and aq. NaOH in COMe_2 give 9-*n*-butylcarbazole-3-carboxylic acid, m.p. 157°. 2-Acetylcarbazole, R_2SO_4 , and NaOH in $\text{COMe}_2\text{-H}_2\text{O}$ give 2-acetyl-9-ethyl-, m.p. 97°, and *n*-butyl-carbazole, m.p. 74·5—75°, converted by fusion with KOH into 9-ethyl-, m.p. 248°, and 9-*n*-butyl-carbazole-2-carboxylic acid, m.p. 198°, not obtained from carbazole-2-carboxylic acid (II) by R_2SO_4 . $\text{HNO}_3\text{-AcOH}$ at 80—85°, followed by NaOH-EtOH- H_2O , converts (II) into 6-nitrocarbazole-2-carboxylic acid, m.p. 338° (? decomp.), decarboxylated by Cu-bronze in crude picolines to 3-nitrocarbazole. Heating cyclohexanone and $p\text{-NH}_2\text{·NH·C}_6\text{H}_4\text{·CO}_2\text{H}$ at 100° and then with 10% H_2SO_4 at 100° gives 5:6:7:8-tetrahydrocarbazole-3-carboxylic acid, m.p. 279°. With hot $\text{OH·[CH}_2\text{]}_n\text{·Cl}$ ($n = 2$ or 3) and HCl, (II) gives β -chloroethyl-, m.p. 141°, and γ -chloropropyl carbazole-3-carboxylate, m.p. 129°. $p\text{-OPh·C}_6\text{H}_4\text{·CHO}$, Ac_2O , and NaOAc yield (boiling) β -*p*-phenoxyphenylacrylic acid, m.p. 135° (chloride, b.p. 225°/18 mm.). γ -Chloropropyl dibenzfuran-3-carboxylate, m.p. 85°, is prepared as above. These intermediates and other appropriate acids give by standard methods the following, m.p. in parentheses being those of hydrochlorides: β -diethyl-aminoethyl carbazole-2-, m.p. 127°, -3- (m.p. 195°), and -1- (an oil), 9-ethylcarbazole-2- (III) (m.p. 174°) and -3- (m.p. 204°), 9-*n*-butylcarbazole-2- (an oil) and -3- (sulphate, a glass), 6-nitrocarbazole-2- (IV) (m.p. 225—227°), 8-aminocarbazole-2- [by Fe-reduction of (IV)], m.p. 146—147°, 5:6:7:8-tetrahydrocarbazole-3- (m.p. 234°), dibenzfuran-3- (m.p. 185°), -2- (m.p. 221°), and -1- (m.p. 210°), 7-aminodibenzfuran-3- (m.p. 255°), dibenzthiophen-3- (m.p. 219°) and -1- (m.p. 213°), Ph_2 ether-4- (m.p. 136°), and Ph_2 sulphide-4- (m.p. 137°) -carboxylate; γ -diethyl-amino-*n*-propyl carbazole-3- (m.p. 169°) and dibenzfuran-3-carboxylate (m.p. 185°); β -di-*n*-butylaminoethyl carbazole-3-carboxylate (m.p. 187°); β -diisobutyl- (m.p. 212°) and β -di-*n*-amyl-aminoethyl dibenzfuran-3-carboxylate (m.p. 160°); β -diethylaminoethyl β -2-dibenzfuryl- (m.p. 185°) and *p*-phenoxyphenyl-acrylate (m.p. 129—130°). The anaesthetic activity (rabbits' cornea) and toxicity (mice) of the NR_2 -esters are recorded and discussed. (III) is the most effective, three times as potent and one fifth as toxic as cocaine. All are irritant to the cornea and when injected subcutaneously (man). R. S. C.

Naphthaquinacridone. V. S. JAKUSCHEVSKI (J. Gen. Chem. Russ., 1939, **9**, 1877—1879).—1:4-



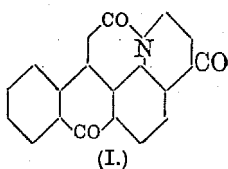
(I.)

Naphthaquinone in AcOH and $o\text{-NH}_2\text{·C}_6\text{H}_4\text{·CO}_2\text{H}$ (2 hr. at the b.p.) yield 1:8- $\text{C}_{10}\text{H}_6(\text{OH})_2$ and naphthaquinacridone (I), which

dyes animal fibres orange in acid solutions, and dyes cotton indigo-blue (alkaline $\text{Na}_2\text{S}_2\text{O}_4$).

R. T.

Polycyclic compounds. I. Anthrapyridone-acridone. A. M. LUKIN and P. M. ARONOVITSCH (J. Gen. Chem. Russ., 1939, **9**, 1774—1776).—



(I.)

1-Acetanilidoanthraquinone-2-carboxylic acid, boiled with 0·8% NaOH for 10 hr., yields *N*-phenyl-1:9-anthrapyridone-2-carboxylic acid, m.p. >300° (decomp.), which gives anthrapyridoneacridone (I), m.p. >300°, when treated with ClSO_3H at 40°. (I) yields a violet vat with alkaline NaHSO_3 . R. T.

Alkaline hydrolysis of condensation products of hydantoin with aldehydes. H. R. HENZE, W. R. WHITNEY, and (Miss) M. A. EPPRIGHT (J. Amer. Chem. Soc., 1940, **62**, 565—568).—Anisylidenehydantoin with 5% aq. NaOH at 80—90° gives $p\text{-C}_6\text{H}_4\text{Me·OMe}$ (I) and $\text{H}_2\text{C}_2\text{O}_4$, also obtained with $p\text{-OMe·C}_6\text{H}_4\text{·CO}_2\text{Me}$ and a trace of $p\text{-OMe·C}_6\text{H}_4\text{·CHO}$ by aq. $\text{Ba}(\text{OH})_2$ at 120—135°. 2-Phenyl-4-*p*-anisyl-oxazolone and 40% NaOH at 110—115° give (I) and $p\text{-OMe·C}_6\text{H}_4\text{·CO·CO}_2\text{H}$, converted by aq. $\text{Ba}(\text{OH})_2$ into (I) and $\text{H}_2\text{C}_2\text{O}_4$. *o*-Chlorobenzylidenehydantoin, m.p. 275°, with $\text{Ba}(\text{OH})_2$ gives *o*- $\text{C}_6\text{H}_4\text{MeCl}$, and with HI·AcOH gives *o*-chlorobenzylhydantoin, m.p. 240°, hydrolysed by $\text{Ba}(\text{OH})_2$ to *o*-chlorophenylalanine, m.p. 260—261° (hydrochloride, m.p. 255—256°). *m*-Nitrobenzylidenehydantoin, m.p. 277°, with $\text{Ba}(\text{OH})_2$ gives *m*- $\text{C}_6\text{H}_4\text{Me·NO}_2$ and $\text{H}_2\text{C}_2\text{O}_4$, and with Sn·HCl at 120° gives *m*-aminobenzylhydantoin hydrochloride, m.p. 270°, hydrolysed by $\text{Ba}(\text{OH})_2$ to *m*-aminophenylalanine (dihydrochloride, m.p. 225°). Furfurylidenehydantoin and $\text{Ba}(\text{OH})_2$ give 2-methylfuran and $\text{H}_2\text{C}_2\text{O}_4$. M.p. are corr. R. S. C.

*iso*Propylbarbital, m.p. 116·7—117·1°, and *isobutyl*barbital, m.p. 109·6—110·3°.—See A., 1940, III, 329.

N-Derivatives of imidazole (glyoxaline). I. S. I. LURIE, M. G. KULESCHOVA, and N. K. KOTSCHETKOV (J. Gen. Chem. Russ., 1939, **9**, 1933—1938).—The Ag salt (I) of glyoxaline with 5-chloro-8-nitro-3-alkoxyacridines, in tetrahydronaphthalene solution at the b.p., yields 8-nitro-5-*N*-glyoxaliny-3-ethoxy-, m.p. 268—269° (decomp.), or -3-methoxy-acridine, m.p. 226—227°. β -Bromoethylphthalimide and (I) in xylene afford *N*- β -glyoxalinyethylphthalimide, which with N_2H_4 in EtOH (3 hr. at the b.p.) gives β -*N*-glyoxalinyethylamine [dihydrochloride (II), m.p. 216—218°]; γ -*N*-glyoxalinypropylamine, m.p. 117—119° [dihydrochloride (III), m.p. 230—232°], is prepared similarly. 5:8-Dichloro-2-methoxyacridine and (II) or (III) in PhOH (3—4 hr. at 150—160°) yield 8-chloro-3-methoxy-5-(β -*N*-glyoxalinyethylamino)-, m.p. 181—182°, or -5-(γ -*N*-glyoxalinypropylamino)-acridine hydrochloride, m.p. 170—172°. $p\text{-NHAc·C}_6\text{H}_4\text{·SO}_2\text{Cl}$ (IV) and (I) in EtOH (1 hr. at the b.p.) give *N*-acetsulphanilylglyoxaline, m.p. 166—167°, which yields glyoxaline, sulphanilic acid, and AcOH when hydrolysed (15% HCl or H_2SO_4). (IV) and (II) in aq. COMe_2 give the β -*N*-glyoxalinyethylamide of acetsulphanilic acid, m.p. 227—228°, hydrolysed (boiling 15% HCl) to sulphanil-(β -*N*-glyoxalinyethyl)amide, m.p. 156—157°. R. T.

Pyrrole series. IV. Dipyrromethene which is a true intermediate in its own formation. J. H. PADEN, A. H. CORWIN, and W. A. BAILEY, jun. (J. Amer. Chem. Soc., 1940, **62**, 418—424; cf. A., 1937, II, 522).—The relative rates of reaction show that the usual dipyrromethene synthesis proceeds by way of the di- to the tri-pyrromethene, which then reverts to the dipyrromethene by fission. The intermediate steps are realised in typical cases. R. S. C.

Thioide, additive compound of piperazine and carbon disulphide. R. CHARONNAT (Atti X Congr. Internaz. Chim., 1938, III, 65—73).—Thioide, $(C_5H_{10}N_2S_2)_x$ (I) (cf. Schmidt *et al.*, A., 1892, 210; Herz, A., 1897, i, 488), from piperazine and CS_2 in EtOH, gives Na, K, and Ag salts, and salts of heavy metals; it also forms a *picrate*, and a *periodide* which is slowly converted into a yellow substance, $C_8H_{12}N_4S_4$. AcOH and dil. HCl decompose (I), which exhibits oxidation-reduction properties. A formula is proposed for (I). E. W. W.

Pyrazine series. II. Preparation and properties of aminopyrazine. S. A. HALL and P. E. SPOERRI (J. Amer. Chem. Soc., 1940, **62**, 664—665; cf. A., 1938, II, 158).—Pyrazine-2:3-dicarboxylic acid at 210°/3—4 mm. gives pyrazine-3-carboxylic acid, m.p. 225° (decomp.), and thence the Me ester, m.p. 59° (lit. 62°), amide, m.p. 189° (lit. 188°), and 2-aminopyrazine, m.p. 117—118° (lit. 110—117°) (Ac derivative, m.p. 133°). Na pyrazinecarbamate, decomp. 257—275°, is isolated as intermediate.

R. S. C.

4:6-Dihydroxy-2-methyl-5-alkylpyrimidines. L. P. FERRIS, jun., and A. R. RONZIO (J. Amer. Chem. Soc., 1940, **62**, 606—607).— $NH:CMc:NH_2 \cdot HCl$ (2.5 mols.), $CHR(CO_2Et)_2$ (R = H or alkyl) (1 mol.), and NaOEt (slightly > 2.5 atoms) in EtOH at room temp. give 4:6-dihydroxy-2-methyl- (absorption max. at 2600 Å.) and -2:5-dimethyl-pyrimidine, 4:6-dihydroxy-2-methyl-5-n-propyl-, -5-n-butyl-, and -5-n-amyl-pyrimidine, sublime at 260—350°. R. S. C.

Selenopyrimidines.—See B., 1940, 246.

Reactions of amidines as ammonio-carboxylic acids or esters. E. C. WAGNER (J. Org. Chem., 1940, **5**, 133—141).—The view that amidines are ammonio-carboxylic acids or esters is established by the production, usually in good yield, of (i) benzimidazoles from $o-C_6H_4(NH_2)_2$ and $NHAr \cdot CH:NAr$ (A) (as with HCO_2H) or $NHAr \cdot CMe:NAr$ (B) (as with AcOH), (ii) quinazolines from $o-NH_2 \cdot C_6H_4 \cdot CO \cdot NHR$ and (A) [as with HCO_2H or $CH(OEt)_3$], (iii) perimidine, m.p. ~238° (picrate, decomp. ~249—250°), from 1:8- $C_{10}H_6(NH_2)_2$ and $NHPh \cdot CH:NPh$ (I) at 160°, and (iv) 1-methylbenzoxazole from $o-NH_2 \cdot C_6H_4 \cdot OH$ and $NHPh \cdot CMe:NPh$ (II) at 190—195°. The reactions with (A) and (B) involve elimination of NH_2Ar (2 mols.). Thus, $o-C_6H_4(NH_2)_2$ (1 mol.) with ~1.5 mols. of (A) (Ar = Ph, *p*-tolyl) at ~125° or phenyl-*o*-tolylacetamide at 180° gives benzimidazole or 2-methylbenzimidazole, respectively. 3-*p*-Tolyl-6-methyl- (III), 6-chloro-3-*p*-chlorophenyl- (IV), and 6-bromo-3-*p*-bromophenyl-3:4-dihydroquinazoline are formed in 20—39% yield from 2:5:1- $NH_2 \cdot C_6H_3R \cdot CH_2 \cdot NH \cdot C_6H_4R \cdot p$ (R = Me, Cl, and Br, M (A., II.)

respectively) and excess of 90% HCO_2H at 100° (bath), and in 48—78% yield with (I); (IV) is also obtained (69%) using (A) (Ar = *p*- C_6H_4Cl). The experiments with (A) were carried out at 130—140° in presence of the amine hydrochloride (probably not necessary). Similar formation of quinazolines could not be effected with (II). $o-NH_2 \cdot C_6H_4 \cdot CO \cdot NHPh$ with boiling HCO_2H or $CH(OEt)_3$ or with (A) (Ar = Ph, *p*- C_6H_4Cl) at 130—160° gives 4-keto-3-phenyl-3:4-dihydroquinazoline, m.p. 139° (corr.) [picrate, m.p. 180.6° (corr.)]; with (II) no quinazoline is isolable. 4-Keto-3:4-dihydroquinazoline [picrate, m.p. 204° (orange to yellow at 180—190°)] is similarly obtained from $o-NH_2 \cdot C_6H_4 \cdot CO \cdot NH_2$ and (A) (Ar = *p*-tolyl). Conversion of 3-*p*-tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline into (III) can be effected with (I) at 190—200° instead of with HCO_2H (cf. A., 1937, II, 520). The compound, m.p. 230—232°, obtained (Rackmann, A., 1910, i, 896) from phenyldiguanide and HCO_2Et in EtOH is also produced using (I) at ~145°. 1:8- $C_{10}H_6(NH_2)_2$ is prepared by reduction ($H_2/30$ lb., Raney Ni, dioxan), which is slow and incomplete, of 1:8- $C_{10}H_6(NO_2)_2$; a dark-blue by-product is also formed. H. B.

Synthesis of pyracridone derivatives. M. I. KABATSCNIK (J. Gen. Chem. Russ., 1939, **9**, 1734—1738).—2:6-Diaminopyridine and $o-C_6H_4Cl \cdot CO_2Na$, heated at 170° for 2 hr. in presence of Cu-bronze and KI, yield *o*-6'-amino-2'-pyridylaminobenzoic acid (hydrochloride, m.p. 253—254°; sulphate, decomp. at 170°), which with conc. H_2SO_4 gives 2-aminopyracridone-5, m.p. 362—363°; this resists the action of boiling 10% NaOH. It is converted via the diazo-compound into 2:5-dihydroxypyracridine, m.p. 373—374°, from which 2:5-dichloropyracridine, m.p. 249.5—251°, is obtained by the action of $POCl_3$. R. T.

Phenylation of oxacarboxyanines. A. T. TROSCHTSCHENKO (J. Gen. Chem. Russ., 1939, **9**, 1661—1665).— $CH(OEt)_3$ in C_5H_5N and the methiodide of 4-, m.p. 217—218°, or 6-phenyl-1-methylbenzoxazole, m.p. 178—180°, yield 4:4', m.p. 235—239°, or 6:6'-diphenyl-2:2'-dimethyloxacarboxyanine iodide, m.p. 243—245°. The above methiodides, when heated with $NHPh \cdot CH:CBR \cdot CHO$ and NaOAc in Ac_2O (3 min. at the b.p.), yield 10-bromo-4:4', m.p. 190—191° (decomp.), or 10-bromo-6:6'-diphenyl-2:2'-dimethyloxacarboxyanine iodide, m.p. 243—245°. R. T.

Attempts to find new antimalarials. XVI. Synthesis of some derivatives of 4-carboline and 5:6-benz-4-carboline. W. O. KERMAK and W. TEBRICH (J.C.S., 1940, 314—318).—3-Chloro-1-methyl-4-carboline methosulphate in molten PhOH with β-diethylaminoethylamine (I), followed by NaOH and then salicylic acid, gives 3-β-diethylaminoethylamino-1:4-dimethylcarbolinium disalicylate (+2H₂O), m.p. 189°; 3-γ-diethylaminopropylamino-1:4-dimethylcarbolinium disalicylate, m.p. 152°, is similarly prepared from the 1:4-Me₂ compound and $NEt_2[CH_2]_3 \cdot NH_2$. 3-Keto-3:4-dihydro-5:6-benz-4-carboline with $POCl_3 \cdot PCl_5$ affords 3-chloro-5:6-benz-4-carboline, m.p. 182°, which with (I) followed by EtOH-HBr yields 3-β-diethylaminoethylamino-5:6-benz-4-carboline di-

hydrobromide, m.p. 270°. 3-Chloro-1-methyl-5:6-benz-4-carboline, m.p. 145°, similarly obtained from the Me derivative, with (I) and EtOH-HCl forms 3-β-diethylaminoethylamino-1-methyl-5:6-benz-4-carboline dihydrochloride (+H₂O), m.p. 261°. 3-Keto-5:6-benz-4-carboline with excess of POCl₃-PCl₅ gives 3:10-dichloro-5:6-benz-4-carboline (II), m.p. 250°. Condensation of *p*-C₆H₄Cl·NH·NH₂ with *o*-nitrophenylpyruvic acid and cyclisation affords 6-chloro-3-*o*-nitrophenylindole-2-carboxylic acid, m.p. 303° (decomp.), reduced and cyclised (Zn-AcOH) to 10-chloro-3-keto-3:4-dihydro-5:6-benz-4-carboline, m.p. 337°, which with PCl₅-POCl₃ forms (II). AcCO₂H and *p*-methoxyphenylmethylhydrazine give the hydrazone, cyclised (HCl) to 5-methoxy-1-methylindole-2-carboxylic acid, m.p. 216°, the acid chloride of which with aminoacetal yields 5-methoxy-1-methylindole-2-carboxydiethylacetamidylamide, m.p. 104°. With HCl-EtOH this is converted into 3-keto-10-methoxy-1-methyl-3:4-dihydro-4-carboline, m.p. 263°, which with POCl₃ and 1 mol. of PCl₅ gives 3-chloro-10-methoxy-1-methyl-4-carboline hydrochloride, m.p. 185°, but with excess of PCl₅, 3:(9:11)-trichloro-10-methoxy-1-methyl-4-carboline, m.p. 214°, is obtained. F. R. S.

New example of dehydrogenating action of thionyl chloride. A. CORBELLINI (Atti X Congr. Internaz. Chim., 1938, III, 82-89).—The action of SOCl₂ on *cis*-*o*-(4:5:1':2'-naphthopyrazolyl)-cinnamic acid (A., 1939, II, 88, 391, 454) is redescribed.

E. W. W.

1:1'-Dithiol-3:3'-bis(isoindolenylidene).—See B., 1940, 192.

Alkyl derivatives of *as*-sulphoxytriazines [5-keto-3-thion-2:3:4:5-tetrahydro-1:2:4-triazine]. E. CATTELAINE (Compt. rend., 1940, 210, 301-303; cf. A., 1939, II, 452).—CH₂Ph·CO·CO₂H with β-alkylthiosemicarbazide (cf. A., 1940, II, 38) gives the β-alkylthiosemicarbazone, which when dissolved in cold NaOH, and then treated with acid, gives 6-benzyl-2-alkylsulphoxytriazine, sol. in Na₂CO₃ and NaHCO₃. The following are prepared: *phenylpyruvic acid* β-methyl-, m.p. ~250° (decomp.) (sublimes at 230-240°), and *benzyl-thiosemicarbazone*, m.p. 174°; 6-benzyl-2-methyl-, m.p. 153.5°, and 2-benzyl-sulphoxytriazine, m.p. 123°.

J. L. D.

Exchange of hydrogen for deuterium in sparingly soluble substances. A. LOEBENSTEIN (Helv. Chim. Acta, 1940, 23, 243-244).—An apparatus is described which operates under diminished pressure and permits the continuous extraction of uric acid (I) with a limited amount of D₂O. (I) contains four replaceable H. 4N-DCI appears to give similar results.

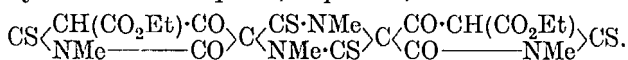
H. W.

Isolation of cyclic peptides from yeast. N. SADIKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1939, 25, 598-600).—When baker's yeast (30 kg.) is heated in 2% aq. Na₂CO₃ to 210° during 3 hr. and then chilled, there are obtained 10 g. of a cyclopeptide, C₂₃H₄₂O₄N₄, m.p. 286-287°, α 0, hydrolysis of which with 37% HCl at 100° gives isoleucine, leucine, and isovaline (2:1:1 mol.).

R. S. C.

Action of methylthiocarbimide on ethyl acetonedicarboxylate. D. E. WORRALL (J. Amer.

Chem. Soc., 1940, 62, 675).—CO(CHNa·CO₂Et)₂ and MeNCS (2 mols.) give *Et* 2:4-diketo-6-thiopiperidine-3-thioform-methylamide-5-carboxylate, m.p. 98° (6-*S*-Me derivative, m.p. 110°) (and a small amount of a substance, C₁₈H₁₄O₅N₄S₄, m.p. 235-236°), converted by Br into the *dispiran*, m.p. 180°.

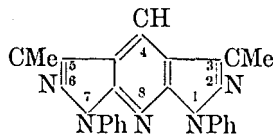


R. S. C.

Preparation of ferric mesoporphyrin chloride. T. H. DAVIES (J. Amer. Chem. Soc., 1940, 62, 447).—Fe^{III} mesoporphyrin chloride is best obtained from Fe^{III} protoporphyrin chloride by hydrogenation (Pd-C) in KOH-MeOH-H₂O and subsequent aeration in AcOH-NaCl at 90°.

R. S. C.

Action of substitution products of carboxylic hydroxyl on methylenepyrroles. G. PERRONCITO (Atti X Congr. Internaz. Chim., 1938, III, 267-276).—1-Phenyl-3-methylpyrazol-5-one (I) (*hydrochloride*, prepared in boiling PhMe) and CH₂(CO₂Et)₂ at 190° give, with a red product, m.p. 170°, α-bis-(5-keto-1-phenyl-3-methyl-4-pyrazolyl)ethyl ether (CMeR₂·OEt, where R = pyrazolyl group), m.p. 281°. With (CH₂·CO₂Et)₂, (I) gives γγ-bis-(5-keto-1-phenyl-3-methyl-4-pyrazolyl)butyrolactone. With NH₂·CHO, (I) gives, at 150-160°, methenylbis-(1-phenyl-3-methylpyrazol-5-one) (cf. A., 1937, II, 307), and, at 200°, "1:7-diphenyl-3:5-dimethylpyridinediazole" [bis-(1'-phenyl-3'-methylpyrazolo-4':5')-3:2:5:6-pyridine] (annexed formula), m.p. (+NH₂·CHO) 155°, of which the 1:3:5:7-Ph₄ analogue [bis-(1':3'-di-



phenylpyrazolo-4':5')-3:2:5:6-pyridine], m.p. (+NH₂·CHO) 175°, is obtained, with methenylbis-1:3-diphenylpyrazol-5-one (III), from 1:3-diphenylpyrazol-5-one (IV). With (CO·NH₂)₂, (I) and (IV) give (II) and (III) respectively.

E. W. W.

isoOxazole chemistry. A. QUILICO (Atti X Congr. Internaz. Chim., 1938, III, 324-345).—A review.

E. W. W.

Transformation of isooxazole-3-carboxylic acids into pyrazole derivatives. III. S. CUSMANO (Gazzetta, 1940, 70, 86-89; cf. A., 1940, II, 55).—5-Methylisooxazole-3-carboxylic acid heated with NPh·NH₂ gives 5-amino-1-phenyl-3-methylpyrazole.

E. W. W.

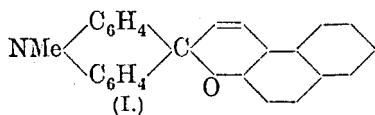
Oximinopyrroles. XIII. **Behaviour with hydroxylamine hydrochloride.** T. AJELLO and S. CUSMANO (Gazzetta, 1940, 70, 127-134).—3-Oximino-2:5-diphenylpyrrole heated with aq. NH₂OH·HCl (I) in MeOH gives, first, αδ-diphenylbutane-αβδ-trione trioxime (II), m.p. 215° (decomp.) [B₃ derivative, m.p. 195° (decomp.)], and then the oxime (III), of 3-benzoyl-5-phenylisooxazole (IV), and 3-phenyl-4-phenacyl-1:2:5-oxadiazole (V) (A., 1938, II, 262). With conc. HCl in MeOH at the b.p., (II) gives (III), followed by (IV). With (I) in MeOH at the b.p., (II) gives (III), and (III) gives (V). 3-Oximino-5-phenyl-2-methylpyrrole heated with (I) in MeOH gives α-phenyl-n-pentane-αγδ-trione trioxime, m.p. 205°, and 3-acetyl-5-phenylisooxazole oxime

(with no oxadiazole). 3-Oximino-2:5-dimethylpyrrole and (I) give *n*-hexane- β - γ -trione trioxime, m.p. 168° (*Bz*₃ derivative, m.p. 180°), which is hydrolysed to the oxime of 3-acetyl-5-methylisooxazole (VI), and to (VI). E. W. W.

New syntheses of isooxazolepolycarboxylic acids. II. III. *iso*Oxazoletricarboxylic acid. L. PANIZZI (Gazzetta, 1940, 70, 89—94, 119—126).—II. CHPh·CH·CCl·N·OH and CO₂Et·CHNa·CO·CO₂Et (I) in MeOH give, after addition of alkali, the *Et*₂ ester (II), b.p. 185°/2—3 mm., of 3-styryliso-oxazole-4:5-dicarboxylic acid (III), m.p. 204—205° (decomp.) (Na₂, K H, Ag₂, Ba, and Pb salts; Me₂ ester, m.p. 82—82.5°; dichloride; diamide, m.p. 219—220°; dianilide, m.p. 235—236°), to which (II) is hydrolysed, by way of 4-carbethoxy-3-styrylisooxazole-5-carboxylic acid, m.p. 156—157°.

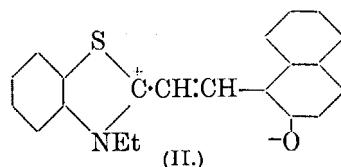
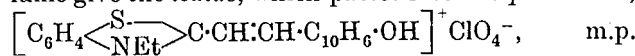
III. The Na₂ salt of (III) with KMnO₄ gives BzOH, some PhCHO, and isooxazole-3:4:5-tricarboxylic acid (IV) (+4H₂O), m.p. (anhyd.) 165—166° (Pb, Ba, and Ag salts). Aq. (IV) (which is unstable) with KCl gives the *K* H₂ salt, decomp. ~124°. CO₂Et·CCl·N·OH and (I) in EtOH, or, better, MeOH, give (with some 3:4-dicarbethoxy-1:2:5-oxadiazole 2-oxide) the *Et*₃ ester (V), b.p. 165—166°/2—4 mm., of (IV), to which (V) is hydrolysed. In boiling dil. H₂SO₄, (IV) gives CO₂, NH₃, and AcCO₂H (mechanism discussed). E. W. W.

Intramolecular ionisation. R. WIZINGER and H. WENNING (Helv. Chim. Acta, 1940, 23, 247—271).—It is shown that all transitions are possible from pyrans which are not ionised under any conditions to spirans (compounded from spiran and betaine) which exist only in the intramol. ionoid form. Apparently intramol. ionisation may occur with all cyclic compounds which contain a sufficiently positivised C attached to an atom which can pass into the negative ionoid state. It can therefore be expected among lactones, lactams, cyclic thio-ethers, and suitably substituted cyclic amines of which there are several examples in the literature. Condensation of CPh₂:CH₂ with 2:1-OH·C₁₀H₆:CHO in HCl-AcOH yields *diphenylnaphthopyran*, m.p. 197°, which has little tendency to add acid and gives an unstable blue colour in AcOH-H₂SO₄; it does not give a colour reaction in boiling Ph₂O. The positivising action of OMe·C₆H₄· is manifest since (OMe·C₆H₄)₂C:CH₂ and *o*-OH·C₆H₄:CHO yield *o*-hydroxystyryldianisylcarbenium perchlorate, decomp. 144°, which only acquires normal intensity in the presence of acid and is converted by H₂O into *dianisylbenzopyran* which could not be obtained cryst. 9:10-Dimethylacridinium methosulphate and 2:1-OH·C₁₀H₆:CHO in boiling AcOH yield, after addition of HClO₄, 9:2'-hydroxybenzostyryl-10-methylacridinium perchlorate, decomp. 280°, which with NH₃ in boiling EtOH affords the colourless 10-methylacridino-2'-naphthopyrrospiran (I), m.p. 233° after becoming blue at 231°, which



gives distinctly blue solutions in boiling EtOH and C₆H₆ and particularly marked effects in boiling 1:2:4-C₆H₃Cl₃; when the solutions are

cooled the colour disappears. 10-Methylacridino-benzopyrrospiran, m.p. 220—221°, is colourless in all indifferent solvents below 250°; with HClO₄ it gives the orange 2'-hydroxystyryl-10-methyl-9-acridinium perchlorate, decomp. 252°. 1:3:3-Trimethyl-2-methyleneindoline and 2:1-OH·C₁₀H₆:CHO in boiling MeOH yield 1:3:3-trimethylindolino- β -naphthopyrrospiran, m.p. 183°, which in cold solvents gives pale reddish-violet solutions becoming more intense when warmed and pale again when cooled; addition of H₂O to the solution in cold C₅H₅N or MeOH intensifies the colour. It gives a deep red solution in AcOH from which HClO₄ ppts. the corresponding perchlorate, m.p. 198—199°. 1:3:3-Trimethylindoleno-benzopyrrospiran, m.p. 208°, similarly derived from *o*-OH·C₆H₄:CHO, is colourless in most boiling solvents but violet in boiling Ph₂O; the colourless solution in boiling C₅H₅N becomes faintly violet on addition of H₂O. It gives a yellow solution in AcOH from which a yellow perchlorate, m.p. 248—249°, separates. More decided intramol. ionisation is shown by the spirans from 5-methoxy-1:3:3-trimethyl-2-methyleneindoline. 5-Methoxy-1:3:3-trimethylindolino- β -naphthopyrrospiran forms colourless crystals, m.p. 151° to a violet-red melt after becoming red at 145°. The cold solutions are more or less red-violet according to the nature of the solvent and pronounced darkening occurs on heating. It gives a red acetate, which passes into the corresponding perchlorate. 5-Methoxy-1:3:3-trimethylindolinenobenzopyrrospiran, m.p. 122°, forms violet solutions which become red on addition of H₂O and, if very dil., orange-yellow on further addition of H₂O owing to production of a hydrate form. The presence of OMe appears to favour intramol. ionisation. 8'-Methoxy-10-methylacridinobenzopyrrospiran, m.p. 159° (corresponding perchlorate, m.p. 210°), is violet in boiling Ph₂O. 8'-Methoxy-1:3:3-trimethylindolinenobenzopyrrospiran, m.p. 122°, is violet in boiling Ph₂O, blue in EtOH, COMe₂, or C₅H₅N, becoming blue-red on addition of much H₂O. 5:8'-Dimethoxy-1:3:3-trimethylindolinenobenzopyrrospiran forms colourless crystals, m.p. 151° to an intensely blue liquid. 1-Ethylbenzthiazolium iodide and 2:1-OH·C₁₀H₆:CHO in boiling EtOH containing piperidine give the iodide, which passes into the perchlorate,



249°, which with NH₃ yields 1-ethylbenzthiazolino- β -naphthopyrrospiran (II), m.p. 186°. Its solutions in indifferent

anhyd. solvents are intensely violet. 1-Ethylbenzselenazolium iodide and 2:1-OH·C₁₀H₆:CHO give a similar iodide and perchlorate, m.p. 203°, which yield 1-ethylbenzselenazolino-2-naphthopyrrospiran, m.p. 183°, and 1-methylquinaldinium methosulphate affords an iodide and perchlorate, m.p. 266°, and 1-methylquinolino-2-naphthopyrrospiran, m.p. 233°. 4:6-Diphenyl-2-methylpyrroliumsulphoacetate and 2:1-OH·C₁₀H₆:CHO in boiling AcOH followed by HClO₄ yield 4:6-diphenyl-2:2'-hydroxybenzostyrylpyrrolium perchlorate, m.p. 236°, converted by warm NH₂Ph into the corre-

sponding 1-phenylpyridinium salt, which with alkali yields 1:4:6-triphenylpyridino-2-naphthopyrrolo-spirain, m.p. 267°. The hydroxyl forms are very readily produced from the last-named two spirains.

H. W.

2:2-Dimethylthiazolidine-5-carboxylic acid, m.p. 165—168°, $[\alpha]_D -75.2^\circ$ to 0° in H_2O in 35.5 hr.—See A., 1940, III, 315.

Action of bromine on thioamides. D. E. Worrall and A. W. Phillips (J. Amer. Chem. Soc., 1940, 62, 424—425).— $NPh:CSH \cdot CH(CO_2Et)_2$ and Br in AcOH give Et_2 1-benzthiazolylmalonate, m.p. 138—139°, which forms a salt with KOH-EtOH, liberates CH_4 from $MgMeI$, and with hot, conc. HCl gives 1-methylbenzthiazole. CH_3Ac_2 and $NPh:CS$ give γ -1-benzthiazolylacetylacetone, m.p. 155°. R. S. C.

Reaction of some acylbenzisothiazolones with acetic anhydride and potassium acetate. E. W. McClelland, M. J. Rose, and (in part) R. G. Bartlett (J.C.S., 1940, 323—327).—1-Propionylbenzisothiazolone, m.p. 144°, prepared from benzisothiazolone and $(EtCO)_2O$, with KOAc and Ac_2O gives 3-hydroxy-2-acetyl-, 3-acetoxy-, 3-acetamido-, and 3-propionamido-1-thionaphthen, m.p. 115° (2-Br-derivative, m.p. 156°; also prepared by propionylation of 3-amino-1-thionaphthen), and 3-hydroxy-2-acetylcarbamyl-1-thionaphthen (I), m.p. 204° (3-Ac derivative, m.p. 130°; also prepared from 2-carboxyphenylthiolacetamide, m.p. 210°, and Ac_2O). 1-Chloroacetylbenzisothiazolone, m.p. 171°, with KOAc and Ac_2O , at 70°, gives 1-acetylbenzisothiazolone, at 95°, (I), and at 115°, 3-hydroxy-2-acetyl- and 3-acetamido-1-thionaphthen: this confirms that the displacement of the 1-substituent takes place in the benzisothiazolone stage. The behaviour of the Bz compound is similar to that of the $EtCO$ derivative. 1-Phenylacetylbenzisothiazolone, m.p. 137°, gives 3-hydroxy-2-acetyl-1-thionaphthen, (I), and 3-phenylacetamido-1-thionaphthen, m.p. 76°. The total or partial displacement of the 1-substituent by Ac in the acyl derivatives is in contrast to the behaviour of the 1-alkyl- or 1-aryl-benzisothiazolones. 2-Nitro-3-benzamido-1-thionaphthen, m.p. 180°, and 3-hydroxy-2-carbamyl-1-thionaphthen, m.p. 208°, are also described.

F. R. S.

Benz-oxazoles and -thiazoles.—See B., 1940, 267.

Isomorphous relationships of organic compounds of analogous constitution. N. M. Cullinane and W. T. Rees (Trans. Faraday Soc., 1940, 36, 507—514; cf. A., 1938, II, 118).—M.p.- and f.p.-composition curves have been determined for binary mixtures containing phenoxazine (I), phenothiazine (II), diphenylene dioxide (III), phenoxthionine (IV), and thianthren (V). (I)-(IV), (I)-(V), (II)-(III), and (III)-(IV) give simple eutectics at 50°, (I) 10 mol.-%: 118°, (V) 45 mol.-%; 103.5°, (II) 16 mol.-%; and 46.5°, (IV) 78 mol.-%, respectively. (II)-(IV) and carbazole-(III) give complete series of mixed crystals with no max. or min. f.p. (I)-(II), (I)-(III), and (II)-(V) each give an incomplete series of mixed crystals with a eutectic. These and other data are discussed from the point of view of mol. shape, and the results indicate that analogously con-

stituted derivatives of elements of similar type form solid solutions, provided that their configurations are also alike.

F. L. U.

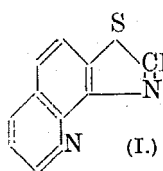
[Condensation of] arylthiocarbimides and ethyl acetonedicarboxylate. D. E. Worrall (J. Amer. Chem. Soc., 1940, 62, 578).—Addition of $CO(CH_3 \cdot CO_2Et)_2$ and then of $ArNCS$ (1 mol. each) to Na (2 atoms) in Et_2O gives Et 2:4-diketo-6-thio-1-phenylpiperidine-3-thioformanilide-5-carboxylate, m.p. 188—189° (decomp.), 1-m-tolylpiperidine-3-thioform-m-toluidide-5-carboxylate, m.p. 125—126° (decomp.), 1-p-anisylpiperidine-3-thioform-p-anisidide-5-carboxylate, m.p. 162—163° (decomp.), 1-p-phenetylpiperidine-3-thioform-p-phenetidide-5-carboxylate, m.p. 195—197° (decomp.), and 1-p-bromophenylpiperidine-3-thioform-p-bromoanilide-5-carboxylate, m.p. 179—181° (decomp.), converted by MeI in $EtOH$ into the 6-methylthiol compounds, m.p. 148—149°, 137—138°, 152—153°, 114—115°, and 152°, respectively, and by Br into 1-2':4'-diketo-6'-thio-5'-carbethoxy-1'-phenyl-3'-piperidyl-, 1'-m-tolyl-3'-piperidyl-4- or -6-methyl-, 1'-p-anisyl-3'-piperidyl-5-methoxy-, 1'-phenetyl-3'-piperidyl-5-ethoxy-, and 1'-p-bromophenyl-3'-piperidyl-5-bromo-thiazole, respectively, m.p. very high (cf. A., 1940, II, 23).

R. S. C.

Preparation of 2':3'-pyridino-3:4-benzthiazole (quinthiazole). H. Erlemeyer and H. Ueberwasser (Helv. Chim. Acta, 1940, 23, 328—332).—Addition of $o\text{-NO}_2 \cdot C_6H_4 \cdot NH_2$ in $CHCl_3$ to a boiling solution of $CSCl_2$ in the same solvent yields $o\text{-NO}_2 \cdot C_6H_4 \cdot NCS$, m.p. 72°, which is converted by $NH_3 \cdot EtOH$ into $o\text{-NO}_2 \cdot C_6H_4 \cdot NH \cdot CS \cdot NH_2$, m.p. 136°. This is transformed by Br in $CHCl_3$ into 2-nitro-1-aminobenzthiazole, m.p. 254° [lit. m.p. 232° (decomp.)], which is dissolved in H_3PO_4 (d 1.7) and treated at $+5^\circ$ with HNO_3 (d 1.4) followed at -15° to -13° by conc. aq. $NaNO_2$; the diazonium solution treated with conc. HCl and Cu gives 1-chloro-3-nitrobenzthiazole, m.p. 169—170°. In this compound Cl is very mobile but unexpectedly is not removed by hydrogenation (Raney Ni in $C_6H_6 \cdot H_2O$), the product being 1-chloro-3-aminobenzthiazole, m.p. 87—89° (yield 74%). This is transformed by red P and HI (d 1.7)-aq. AcOH into 3-amino-1-benzthiazole, m.p. 94°, which with As_2O_5 , glycerol, and conc. H_2SO_4 affords 2':3'-pyridino-3:4-benzthiazole (quinthiazole) (I), m.p. 158°, which does not appear to give a hydrate.

H. W.

Heterocyclic thioindigotin dyes. I. Synthesis of bis-(5:6-quinolino-oxythiophen)indigotin. S. Maruyama (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 1165—1177).—6-Carboxyquinoline-5-diazonium chloride (I) condenses directly, or through the 5-Cl-compound, with thioglycolic acid to give 6-carboxyquinoline-5-thioglycollic acid (II) in poor yield. (I) with Na_2S_2 gives bis-(6-carboxy-5-quinolyl) disulphide and 6-carboxy-5-quinolyl sulphide; the former is not reduced with $K_2S_2O_4$. (I) is converted through the thiocyanate with $H_2S \cdot NaOH$, or through the Et 5-thiolthioncarboxylate with $NaOH$, into 5-thiolquinoline-6-carboxylic acid, which is converted



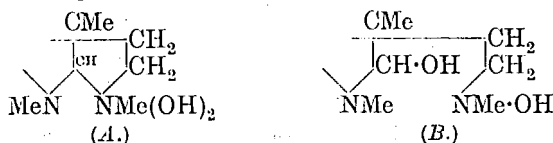
into (II) and thence with O_2 -hot AcOH into *bis*-(5 : 6-quinolino-oxythiophen)indigotin, m.p. 400—410°.

J. L. D.

Two degradation products of hæmocyanin. M. FLORKIN and C. TOUSSAINT (Compt. rend. Soc. Biol., 1939, **132**, 45—47).—Conant's derivative (A., 1930, 1304) gives a green coloration with orcinol which is not given by that of Schmitz (A., 1931, 497) and is due to the presence of a S compound ($C_7H_{15}O_5N_2S_2$).

H. G. R.

Structure of amine oxides. II. Tautomerism of geneserine. M. POLONOVSKI (Atti X Congr. Internaz. Chim., 1938, III, 306—311).—Geneserine (I), although the *N*-oxide of eserine, has reducing properties that this lacks; e.g., (I) reduces methylene-blue (action inhibited by strong acids or their salts). It is suggested that (I) is a tautomeride of *N*-oxide (A) and hydroxylamine (B) forms, of the annexed partial structures.



With SO_2 , (A) gives eserine sulphate, and (B) a sulphaminic acid.

E. W. W.

Alkaloids of the Papaveraceæ family. V. Alkaloids of *Roemeria refracta*, D.C. Structure of roemerine. S. JUNUSOV, R. A. KONOVALOVA, and A. P. ORÉKHOV (J. Gen. Chem. Russ., 1939, **9**, 1868—1876, and Bull. Soc. chim., 1940, [v], **7**, 70—77; cf. A., 1939, II, 565; 1940, II, 111).—Roemerine (I) is demethylenated when heated with phloroglucinol and HCl (6 hr. at 140—150°) giving *nor-roemerine*, m.p. 162—164° [*hydrochloride*, m.p. 210—220°; Me_2

ether, m.p. 165—166° [*hydrochloride*, m.p. 242—243°; *methiodide* (II), m.p. 164—167°]. (II), heated with KOH in MeOH, yields 5 : 6-dimethoxy-8-vinylphenanthrene (III), m.p. 86—87°, together with dimethylde-*N*-methyl-*nor-roemerine*, an oil, $[\alpha]_D^{25} +13.55^\circ$ in EtOH, the *methiodide*, m.p. 278°, of which gives (III) when treated with KOH-MeOH. (III) is oxidised ($KMnO_4$) to 3 : 4-dimethoxyphenanthrene-1-carboxylic acid, m.p. 212—213°. (I) is therefore (A).

R. T.

Aconitum alkaloids. I. Alkaloids of *Aconitum talassicum*. R. KONOVALOVA and A. ORÉKHOV [with A. FILINA] (Bull. Soc. chim., 1940, [v], **7**, 95—105).—The dried roots of *A. talassicum*, moistened with 10% NH_3 and extracted with boiling $(CH_2Cl)_2$, give a mixture of alkaloids (1.5% of the wt. of plant) from which by fractional pptn. of the perchlorates etc. the following bases are isolated: *talatisine* (I), $C_{20}H_{29}O_3N$, m.p. 246—246.5° (decomp.), $[\alpha]_D^{25} +37.7^\circ$ in abs. EtOH [*hydrochloride*, m.p. 256—257°; *picrate*, m.p. 257—260° (decomp.); *perchlorate*, m.p. 220° (decomp.); *hydriodide*, m.p. 265—266° (decomp.)], which contains 3 OH since it yields a *tri*-

acetate, m.p. 211—212° [*perchlorate*, m.p. 165—166°; *methiodide*, m.p. 253—254° (decomp.)], hydrolysed to (I) and is converted by $SOCl_2$ into *talatisine trichloride*, $C_{20}H_{26}NCl_3$, m.p. 175—176°, $[\alpha]_D^{25} +8.6^\circ$ in MeOH: *talatisamine* (II), $C_{22}H_{25}O_4N$, m.p. 144—146°, $[\alpha]_D^{25} \pm 0^\circ$ (hygroscopic *hydrochloride*, m.p. 195—196), which gave no picrate, picrolonate, or perchlorate, does not unite with MeI, and does not give cryst. compounds with Ac_2O or $BzCl$: *talatisidine* (III), m.p. 220—221°, $[\alpha]_D^{25} -20.0^\circ$ in $COMe_2$ [*perchlorate*, m.p. 218—220°; *hydrochloride*, m.p. 186—189°; *picrate*, m.p. 161—164° (decomp.)]; *isotalatisidine* (IV), $C_{23}H_{37}O_5N$, m.p. 139—140°, which gave no cryst. salts. Comparison of the formulæ of (I), (II), (III), and (IV) suggests that they are derived from the same fundamental nucleus $C_{19}H_{28}NH$ or $C_{19}H_{29}N$ although the presence of certain substituents is yet unproven. This same nucleus appears to be present in aconitine, mesaconitine, hypaconitine, pseudaconitine, indaconitine, bitetraconitine, and lappaconitine.

H. W.

Alkaloids of *Girgensohnia diptera*, Bge., Chenopodiaceæ family. N. K. JURASCHEVSKI and S. I. STEPANOV (J. Gen. Chem. Russ., 1939, **9**, 2203—2206).—The air-dry plant contains 1.25% of alkaloids, from which *N*-methylpiperidine and *dipterine*, $C_{11}H_{14}N_2$, m.p. 87—88° $[\alpha]_D^{25} 0$ (*hydrochloride*, m.p. 177—178°; *picrate*, m.p. 189—190°; *platinochloride*, m.p. 167—169°; *picrolonate*, m.p. 242—243°), were isolated.

R. T.

Lupine. XV. Alkaloids of *Lupinus sericeus*, Pursh. J. F. COUCH (J. Amer. Chem. Soc., 1940, **62**, 554—556; cf. A., 1940, II, 111).—This plant (whole) yields spathulatine (I) and *nonalupine* (II), $C_{15}H_{24}ON_2$, m.p. (+2H₂O) 91.5—92.5°, (anhyd.) 235° (softens at 219°), b.p. 260—270°/18 mm. [*aurichloride*, m.p. 177.5—178° (decomp.); *picrate*, m.p. 185—186°]. The formula (A., 1925, i, 61) of (I) (compound, $B, 3KI$, m.p. 260—261°) is confirmed. (I) contains 3 $N \rightarrow O$ groups and with SO_2 gives an oil; with boiling 10% HCl it gives an oily isomeride, $C_{15}H_{24}N_2$ (*perchlorate*, m.p. 216—217°; *picrate*, m.p. 214—216°), of spartyrine, probably by hydrolysis and subsequent ring-closure. Mineral acids do not give salts with (II), which contains no $N \rightarrow O$ (unaffected by SO_2) and with cold, aq. $KMnO_4$ gives *oxymonalupine*, $C_{15}H_{24}O_3N_2$, m.p. 168.5—170.5° (*aurichloride*, m.p. 238—239°), unaffected by SO_2 .

R. S. C.

Alkaloids of *Sedum acre*, L. D. G. KOLESNIKOV and A. G. SCHVARTZMAN (J. Gen. Chem. Russ., 1939, **9**, 2156—2157).—The air-dry plant contained 0.3% of alkaloids, including sedamine, $C_{17}H_{24}O_2N$, m.p. 86—87°, $[\alpha]_D^{25} -56.75^\circ$ in MeOH. Sedamine contains one NMe and one OH.

R. T.

Erythrina alkaloids. VII. Isolation and characterisation of new alkaloids, erythraline and erythratine. K. FOLKERS and F. KONIUSZY (J. Amer. Chem. Soc., 1940, **62**, 436—441; cf. A., 1940, II, 29).—Crystallisation of the hydriodides of the crude alkaloids from seeds of *E. glauca*, Willd., yields *erythraline* (I), $C_{18}H_{19}O_3N$, m.p. 106—107°, $[\alpha]_D^{25} +211.8^\circ$ in abs. EtOH [*hydriodide*, m.p. 252—253° (decomp.)], $[\alpha]_D^{25} +177^\circ$ in H_2O ; *hydrobromide*, m.p. 243°, $[\alpha]_D^{25} +216.6^\circ$ in H_2O], with smaller amounts

of erythramine (II) and *erythratine* (III), $C_{18}H_{21}O_4N$, $+0.5H_2O$ (retained at $140^\circ/0.1$ mm.), m.p. $170-170.5^\circ$, $[\alpha]_D^{25} +144.9^\circ$ in abs. EtOH (best isolated from EtOH as free base; *hydriodide*, m.p. $242-242.5^\circ$, $[\alpha]_D^{25} +109.0^\circ$ in H_2O); *hydrobromide*, m.p. 241° , $[\alpha]_D^{25} +158.7^\circ$ in H_2O). (I) is isolated also from 5 other *Erythrina* species. Hypaphorine is isolated from 5 *Erythrina* species, and it and (I) exist also in 2 further species. The curare-like activity (frogs) of (I) and (II) is the same (dose = 7–8 mg. per kg.), but that of (III) is one tenth as great. R. S. C.

Erythrophleum alkaloids. I. Erythrophleine. B. K. BLOUNT, H. T. OPENSHAW, and A. R. TODD (J.C.S., 1940, 286–290).—Erythrophleine (I) (amorphous), from the bark of *E. guineense*, G. Don., is probably $C_{24}H_{39}O_5N$. Hydrolysis (boiling $N/3-H_2SO_4$) of (I) gives *erythrophleic acid* (II), $C_{22}H_{32}O_5$, m.p. 218° , $[\alpha]_D^{20} -40^\circ$ in $CHCl_3$, and $NMe_2[CH_2]_2OH$ (*picrate*, m.p. 148° ; *N-methyl-N-β-hydroxyethyl-N'-α-naphthylthiocarbamide*, m.p. 125°). *Me erythrophleate*, amorphous, forms a 2 : 4-dinitrophenylhydrazone, m.p. 219° . (II) contains CO, OH, and OMe; since it also contains one double bond, probably $\alpha\beta$ to CO_2H , it must have three rings. Se-dchydrogenation of (II) affords 1 : 7 : 8-trimethylphenanthrene and a substance, $C_{19}H_{16}Se$, m.p. $161-162^\circ$. Possibly (II) is diterpenoid and (I) is its β -methylaminoethyl ester. F. R. S.

Alkaloids of Fritillaria sewerzowii. S. JUNUSOV, R. KONOVALOVA, and A. ORÉKHOV (J. Gen. Chem. Russ., 1939, 9, 1911–1914).—The air-dry tubers of this Central Asiatic plant contained 0.9% of alkaloids. A new alkaloid, *alginine*, $C_{23}H_{39}O_3N$, m.p. $271-272^\circ$, $[\alpha]_D +108.5^\circ$ in EtOH (*hydrochloride*, m.p. $323-325^\circ$; *methiodide*, m.p. $310-311^\circ$), was isolated; it contains a ternary N, and three OH.

R. T.

Alkaloids of white hellebore. IV. Veratramine, a new alkaloid of white hellebore (Veratrum grandiflorum, Loes., fl.). K. SAITO (Bull. Chem. Soc. Japan, 1940, 15, 22–27; cf. A., 1936, 870).—The “resinous matters” (*loc. cit.*) are dissolved in EtOH and treated with $2N-Ca(OAc)_2$, thus causing separation of Ca chelidonate, which is removed. Addition of NH_3 to the filtrate liberates the alkaloids, which are converted into their sulphates by $2N-Na_2SO_4$ in $0.5N-AcOH$. These are decomposed by Na_2CO_3 in boiling EtOH and jervine is separated as the hydrochloride, which dissolves sparingly in EtOH. The mother-liquors contain *veratramine* (I), which is separated as the sulphate. (I), $C_{26}H_{35}O_2N.H_2O$, has m.p. $209.5-210.5^\circ$, $[\alpha]_D^{20} -70^\circ$ in MeOH (for anhyd. material). It dissolves sparingly in dil. acids and gives a *hydrochloride*, m.p. 310° , and a *picrate*, m.p. $217.5-218^\circ$. The presence of a double linking is established by Wijs' method and by hydrogenation (PtO_2 in glacial AcOH) to *dehydroveratramine*, m.p. $197-198^\circ$. (I) does not contain NMe, OMe, or O_2CH_2 . It behaves as a *sec.* amine. When treated with Na_2CO_3 and MeI it yields *methylveratramine methiodide*, m.p. 268° (corresponding *methochloride*, m.p. 277°). (I) is transformed by boiling Ac_2O into a neutral Ac_3 derivative (III), m.p. $205.5-206^\circ$, which is hydrolysed (KOH–EtOH) to a *compound*, m.p. $179-180^\circ$, $[\alpha]_D^{20} +7^\circ$, from which (II) is re-formed by

Ac_2O . (I) is unchanged by KOH–EtOH. (I) is insol. in aq. NH_3 , Na_2CO_3 , or NaOH, does not give a colour with $FeCl_3$, and does not react with CH_2N_2 ; it therefore does not contain a phenolic OH. It does not react with NH_2OH or $NH_2CO.NH.NH_2$. One of the two O is therefore present in an alcoholic OH and the other appears to be in an indifferent bridge.

H. W.

Phytochemistry of the bark of Tabernaemontana coronaria. A. N. RATNAGIRISWARAN and K. VENKATACHALAM (Quart. J. Pharm., 1939, 12, 174–181).—The EtOH extract of the bark of the stem and root of *T. coronaria* yields fatty matter giving palmitic, cerotic, and oleic acids on saponification, a cryst. resin alcohol, $C_{17}H_{32}O_4$, m.p. $180-181^\circ$, $[\alpha]_D^{20} +87.2^\circ$ in C_6H_6 ($c=0.69$), $+82.87^\circ$ in $CHCl_3$ ($c=2.24$), caoutchouc, resins, sugars, KNO_3 , KCl, and two alkaloids *tabernaemontanine* (I), $C_{20}H_{26}O_3N_2$, m.p. $208-210^\circ$ after sintering at 203° , and *coronarine* (II), $C_{44}H_{56}O_6N_4.2.5H_2O$, m.p. $196-198^\circ$ after sintering at 183° . (I) and (II) are pharmacologically active, showing a definite slowing of the rate and an increase in the amplitude of the beats when applied to a frog's heart *in situ*. (II) gives a green fluorescence when dissolved in EtOH, Et_2O , or $CHCl_3$. Colour reactions of (I) and (II) are described. 17 kg. of bark yield 0.05 g. of alkaloids. F. H.

2(3)-Nitrophenylene-1 : 4-diarsinic acid. A. J. BERLIN (J. Gen. Chem. Russ., 1939, 9, 1856–1857).—3-Nitro-4-aminophenylarsinic acid is diazotised, and Na_3AsO_3 and $CuSO_4$ are added. The solution is filtered after 24 hr., and aq. $NaHSO_3$ is added, followed by H_2SO_4 , and the solution is heated until evolution of SO_2 ceases. The dried ppt. of 2-nitrophenylene-1 : 4-diarsenious oxide (I), m.p. 340° (decomp.), suspended in $CHCl_3$, is saturated with HCl, so giving 2-nitrophenylene-1 : 4-dichloroarsine, 2 : 1 : 4- $NO_2.C_6H_3(AsCl_2)_2$, m.p. 73° , readily converted into pure (I) by the action of NH_3 in $COMe_2$. Cl_2 passed through a suspension of (I) in H_2O , gives 2-nitrophenylene-1 : 4-diarsinic acid. R. T.

Conversion of bismuth aryl halides into bismuth triaryl compounds. H. GILMAN and H. L. YABLUNKY (J. Amer. Chem. Soc., 1940, 62, 665–666).— $BiAr_2Cl$ and $BiAr_3Cl_2$ are best converted into $BiAr_3$ by $N_2H_4.H_2O$ in EtOH. R. S. C.

Action of Grignard reagents on heavy-metal salts. IV. Mechanism of the reaction with silver bromide. E. A. BICKLEY [with J. H. GARDNER] (J. Org. Chem., 1940, 5, 126–132; cf. A., 1940, II, 121).—Decomp. of, e.g., Ag aryls occurs by a bimol. reaction not involving free radicals. The unimportance of solvent is shown by decomp. of a mixture of Ag *p*-tolyl and *p*-anisyl at 100° ; treatment of the resulting product with HI (const. b.p.) gives 4 : 4'-dimethyl-, 4 : 4'-dihydroxy-, and 4-hydroxy-4'-methyl-diphenyl, indicating that all possible coupling products are formed. Furthermore, decomp. of AgPh in CCl_4 , PhCl, or $PhNO_2$ affords only Ph_2 . The relative velocities of the reactions between various Grignard reagents and AgBr are determined indirectly by reaction between pairs of $MgRHal$ and half the amount of AgBr theoretically required to react with them; the amount of each radical coupled is found by

isolating the reaction products. The following order is thus found: $\text{MgPhI} < \text{MgPhBr} < \text{MgBu}^a\text{Br} < \text{MgBu}^a\text{Cl} < \text{MgBu}^a\text{I}$. The results obtained in experiments in which AgBr is present in excess thus become understandable. Thus, with MgPhHal and MgBu^aHal , the largest yield of PhBu^a is obtained when $\text{Hal} = \text{Br}$ in each case, *i.e.*, reaction velocities with AgBr most nearly equal. The amounts of $(\text{CHMeEt})_2$, $\text{CH}_2\text{Ph}\cdot\text{CHMeEt}$, and $(\text{CH}_2\text{Ph})_2$ obtained from $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ (0.5 mol.), $\text{CHMeEt}\cdot\text{MgHal}$ (Cl , Br , I) (0.5 mol.), and AgBr (1 mol.) are determined. The following side reactions are shown to occur: (i) $\text{AgBu}^a + \text{MgI}_2 \rightarrow \text{Bu}^a\text{I} + \text{Ag} + \text{MgI}$; ? (ii) $2\text{AgPh} + \text{MgI}_2 \rightarrow \text{PhI} + \text{MgPhI} + 2\text{Ag}$; no evidence of similar reactions is noted with other halides. H. B.

Germicidal mercury derivatives of pyridine. M. W. SWANEY, M. J. SKEETERS, and R. N. SHREVE (Ind. Eng. Chem., 1940, **32**, 360—363).—Interaction of $\text{Hg}(\text{OAc})_2$, $\text{C}_5\text{H}_5\text{N}$, and H_2O (1 : 8 : 8 mols.) at 155° for 2.5 hr. yields 3-pyridylmercuric acetate (I), m.p. 178° [chloride (II), m.p. 280° ; nitrate (III), explodes $308\text{—}309^\circ$]. Absence of H_2O , or a longer reaction period, causes lower yields of (I) and formation of polymercurated compounds. Similarly are prepared 2-amino- (IV), m.p. 197.5° , and 2-methyl-5-pyridylmercuric chloride (V). Growth of *Staphylococcus aureus* is prevented by (II) at 0.5 p.p.m., by (I) and (III) at 0.6 p.p.m., by (IV) at 1.6 p.p.m., and by (V) at 2.5 p.p.m. Growth of *B. coli* is prevented by (II) at 1.8 p.p.m., and by (I) and (III) at 2.5 p.p.m. The lethal dose of (II) for rats and mice is 53 mg. per kg. body-wt. and of (I) and (III), 17—18 mg.

J. D. R.

Reaction of lead tetraphenyl and bismuth triphenyl with monocarboxylic acids. I. Action of formic and acetic acid on PbPh_4 and BiPh_3 . M. M. KOTON (J. Gen. Chem. Russ., 1939, **9**, 2283—2286).— PbPh_4 and $\text{R}\cdot\text{CO}_2\text{H}$ ($\text{R} = \text{H}$, Me), heated at $50\text{—}150^\circ$, yield C_6H_6 and $(\text{R}\cdot\text{CO}_2)_2\text{PbPh}_2$; under these conditions BiPh_3 gives C_6H_6 and $(\text{R}\cdot\text{CO}_2)_3\text{Bi}$. PbPh_4 or BiPh_3 and HCO_2H at $175\text{—}200^\circ$ give C_6H_6 , CO , CO_2 , and Pb or Bi .

R. T.

Models of protein molecules. D. L. TALMUD (Compt. rend. Acad. Sci. U.R.S.S., 1939, **25**, 484—487).—A polypeptide, built up of NH_2 -acids of the same configuration, has the side chains all on one side of the main chain. By mutual interaction of the side chains, this results in a "ring chain" unit of mol. wt. 693—744, which is the fundamental unit of proteins. These units can unite by loss of H_2O from $\text{NR}\cdot\text{CR}\cdot\text{OH}$ and $\text{NHR}\cdot\text{COR}$ and thus form more complex structures. Such models best account for the properties of proteins.

R. S. C.

Action of benzyl alcohol on peptides and proteins. J. OVERHOFF (Atti X Congr. Internaz. Chim., 1938, III, 263—267).—Glycine and alanine with $\text{CH}_2\text{Ph}\cdot\text{OH}$ (I) at 200° undergo partial decomp. to NH_3 and CO_2 . Glycine anhydride crystallises unchanged from (I). When the NH_2 -group is protected, CH_2Ph esters are readily formed: *e.g.*, hippuric acid heated with (I) gives its CH_2Ph ester (II), m.p. 91° . Aspartic acid is unchanged. Glutamic acid gives benzyl pyrrolidonecarboxylate, b.p. $205^\circ/0.2$ mm.

Benzoylglycylglycine gives its CH_2Ph ester and (II). Peptide linkings are broken by hot (I). With (I) at 210° , gelatin gives $\text{NH}_3 = 2\%$ of the total N and a solution from which Et_2O ppts. an amorphous product (III) (13.7% N; weak biuret reaction). (III) must consist largely of CH_2Ph esters. It is feebly acid; the product benzoylated in $\text{C}_5\text{H}_5\text{N}$ is fairly strongly acid. After hydrolysis by dil. KOH , and acidification, the Bu^aOH extract of the evaporate, when treated with $\text{H}_2\text{O} + \text{Ag}_2\text{O}$, gives proline. Casein is also sol. in (I). E. W. W.

Intramolecular folding of polypeptide chains in relation to protein structure. H. NEURATH (J. Physical Chem., 1940, **44**, 296—305).—The space requirements and orientation of NH_2 -acid residues in fully extended, folded, and cyclised polypeptide chains are discussed. The structures of fully extended chains can account almost quantitatively for observed film areas and properties of protein monolayers. The introduction of NH_2 -acid residues into folded chains is impossible except in certain cases, *e.g.*, glycine and alanine, unless unreasonable distortion of bond angles is assumed. Similarly cyclised chains do not permit the introduction of any side-chains.

C. R. H.

Standardisation of organic combustion furnaces. E. CATTELAINE and R. GROS (Ann. Chim. Analyt., 1940, [iii], **22**, 68—69).—The chief conditions to which the parts of French combustion apparatus ought to conform are laid down.

L. S. T.

Ash in organic compounds. Determination by micro-technique with automatic combustion. A. R. NORTON, G. L. ROYER, and R. KOEGEL (Ind. Eng. Chem. [Anal.], 1940, **12**, 121—123).—An automatic electric micro-furnace in which two samples ($\sim 100\text{—}150$ mg.) can be ashed in a stream of O_2 either simultaneously or individually is described. Comparative data with the muffle macro-method show that the micro-method is quicker and more accurate.

L. S. T.

Direct [semi-micro-]determination of oxygen in organic substances. M. SCHÜTZKE (Z. anal. Chem., 1939, **118**, 245—258).—The org. compound is decomposed by heat, and the products are led in N_2 over C at 1000° , whereby all the O. combined or free, is converted into CO , which is then oxidised to CO_2 at room temp. by a patent prep. the basis of which is I_2O_5 , or by I_2O_5 at 160° as described previously (B., 1940, 356). The CO_2 is absorbed in a Pregl tube with a special filling. The specially filled oxidation tube lasts for ~ 80 analyses. N, S, and halogens do not interfere with the method, and there is no difficulty in analysing liquids. Metal salts that give oxides or carbonates stable at 1000° , *e.g.*, NaOBz , yield low results, but compounds with the metal in SO_3H give correct results for O. Full details of apparatus and procedure are recorded.

L. S. T.

Micro-analytical adaptation of the direct determination of oxygen in organic substances. W. ZIMMERMANN (Z. anal. Chem., 1939, **118**, 258—263).—Details for the conversion of Schütze's semi-micro-method (see above) into an automatic micro-method are given. Test data are recorded.

L. S. T.

Determination of halogens, particularly of iodine, in organic compounds by means of the bomb calorimeter. B. LONGO (Atti X Congr. Internaz. Chim., 1938, III, 427—428).—Compounds difficult to oxidise with HNO_3 are heated in a bomb calorimeter under a pressure of 20—30 atm. of O_2 , and after reduction of iodates formed with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, an aliquot part of the product is used for the volumetric determination of total halogen. A second portion is treated by Gooch's method to eliminate I, and Cl and Br are determined. A third part can be used for the separate determination of Br and Cl. The method has been applied to a large no. of aliphatic and aromatic compounds. J. W. S.

Furnace for micro-Carius determination.—See A., 1940, I, 233.

Determining the composition of mixtures by thermal analysis.—See A., 1940, I, 230.

Determination of vitamin-A and carotene.—See A., 1940, III, 321.

Determination of arginine with flavianic acid. H. B. VICKERY (J. Biol. Chem., 1940, 132, 325—342).—Acid protein hydrolysates are boiled with C, filtered, and 4—5 mols. of flavianic acid are added (as solid) at room temp. On keeping for 4 days in the cold arginine diflavianate separates. It is washed with saturated aq. arginine monoflavianate, suspended in hot H_2O , and 5N-aq. NH_3 is added just to effect dissolution. To the boiling solution N- H_2SO_4 is added, sufficient to neutralise the 5N- NH_3 used; the arginine monoflavianate crystallises, and is collected, washed with EtOH, dried, and weighed. Multiplying by the factor 0.3566 gives the wt. of arginine. Results for some representative proteins are given, and are somewhat > those given by the Ag pptn. method. P. G. M.

Effect of dipolar substituents rich or poor in residual valencies on addition reactions of phenol derivatives with pyridine and esters and amides of pyridine-2- and -3-carboxylic acid. R. LABES (Arch. exp. Path. Pharm., 1938, 190, 421—451).—The pptg. power of phenols for $\text{C}_5\text{H}_5\text{N}$, Et picolinate and nicotinate is increased by the phenol substituent in proportion as the solubility in H_2O is decreased. As $\text{C}_5\text{H}_5\text{N}$ substituent the CO_2Et group is most active in position 3. The ester group decreases the basicity in the $\text{C}_5\text{H}_5\text{N}$ partner. The greatest deviation from the H_2O -solubility rule of the phenol substituents are shown by $\text{NH}_2\cdot\text{CO}$, OH, and NO_2 groups, which are rich in residual valency. The introduction of the $\text{NH}_2\cdot\text{CO}$ group into the $\text{C}_5\text{H}_5\text{N}$ partner also profoundly modifies the effect. With these groups rich in residual valencies the position of the substituents in both partners has a strong influence on the result. J. H. B.

Determination of acetylsulphapyridine.—See A., 1940, III, 435.

Colorimetric determination of hippuric acid. G. DENIGÈS (Compt. rend., 1939, 209, 972—974).—Hippuric acid (I) (0.05%; 5 c.c.) with NaOBr (2 c.c.) (cf. A., 1889, 139) at 100° (bath) 20 min. gives a red ppt. which when extracted with a known vol. of

CHCl_3 or Et_2O yields a red solution, the depth of colour being compared with that given by a standard solution of (I). 0.02% (I) (5 c.c.) gives a perceptible colour. BzOH does not interfere. NaOCl gives a similar, though less sensitive, reaction. J. L. D.

Comparison of colorimetric methods for the determination of nicotinic acid. W. R. ASHFORD and R. H. CLARK (Trans. Roy. Soc. Canada, 1939, [iii], 33, III, 29—32).—The method of Karrer *et al.* (A., 1938, II, 302; III, 1026) as modified by Vilter *et al.* (A., 1938, III, 919) is quite unreliable for determining nicotinic acid (I). The colour fades rapidly, many other compounds interfere, and Et_2O used to remove the excess of 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ also removes some of its product with (I). In the method of Swaminathan (B., 1938, 974), results are affected by p_{H} (best 6.5—7.0), and piperidine, pyrrole, quinoline (II), 2-methylquinoline (III), $\text{C}_5\text{H}_5\text{N}$ (IV), and furfuraldehyde (V) interfere. The colour produced fades more rapidly in conc. than in dil. solutions. Extraction of the coloured complex by *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ is not practicable. The use of $\text{Pb}(\text{OAc})_2$ to remove protein is unsatisfactory, some (I) being adsorbed. The best method is that of Bandier *et al.* (A., 1939, II, 196), with which, however, (II)—(V) interfere.

E. W. W.

Application of electrodialysis to isolation of alkaloids. I. From certain raw materials and their pharmaceutical products. II. In toxicological analysis for strychnine. P. OFICJALSKI (Wiad. Farm., 1939, 66, 145—148, 161—165).—The alkaloids of *Strychnos* seeds, cinchona bark, and sarsaparilla root are quantitatively isolated from suspensions of the material in aq. AcOH by electrodialysis; the same procedure is applicable to determination of strychnine in animal organs. The method does not give satisfactory results in the cases of morphine, cocaine, atropine, and ergot alkaloids, owing to oxidation and/or hydrolysis. R. T.

Kjeldahl determination of nitrogen in some alkaloids in presence of complex mercury, copper, and selenium catalysts. I. General. II. Experimental results. B. DREVON and ROUSSIN (J. Pharm. Chim., 1940, [ix], 1, 18—24, 24—31).—I. A review of the literature (cf. Poe *et al.*, A., 1935, 876, etc.).

II. A catalyst of $\text{HgO} + \text{CuSO}_4\cdot 5\text{H}_2\text{O} + \text{Na}_2\text{SeO}_3$ added to the H_2SO_4 in the Kjeldahl determination of N in various alkaloids, using apparatus similar to that of Guillaume (A., 1927, 887) and Polonovski *et al.* (A., 1935, 1436), has no advantage over previous methods. That of Fleury *et al.* (A., 1924, ii, 273; 1925, ii, 66) remains the most satisfactory with morphine. E. W. W.

Determination of histidine. R. J. BLOCK (J. Biol. Chem., 1940, 133, 67—69).—Histidine (I) in protein hydrolysates is determined by pptn. as Ag salt at p_{H} 7.4, followed by fission of the Ag salt with H_2SO_4 , removal of Ag with H_2S , and pptn. of (I) as an insol. salt with nitranilic acid. J. D. R.

Salting out of amino-acids from protein hydrolysates. Isolation of *l*-phenylalanine.—See A., 1940, III, 421.

A., II.—Organic Chemistry

JUNE, 1940.

Elimination and metathetical reactions and the electronic theory of rearrangements. C. R. HAUSER (J. Amer. Chem. Soc., 1940, 62, 933—941).—Eliminations, metatheses, and rearrangements of org. compounds containing OH or halogen are discussed. Those effected by electron acceptors (acids, heavy-metal salts) occur according to Whitmore's views, except that all the postulated steps may be simultaneous. Eliminations effected by bases occur by removal of H as proton, release of X (= halogen or OH) with a complete octet of electrons, and stabilisation of the mol. With strong bases (type I reactions) removal of H occurs before the other steps, but with weak bases (type II reactions) all three steps may be simultaneous. In a three-atom system stabilisation occurs by rearrangement to unsaturated products or by dimerisation, but in a two- or four-atom system unsaturated compounds are produced without rearrangement. Exchange reactions may occur as well as elimination, the anionic reagent attacking the C at the face most removed from X. Reactions of CO-compounds and their hydrates with bases are discussed in detail. R. S. C.

Bromination of propane. A. GUYER and A. RUFER (Helv. Chim. Acta, 1940, 23, 533—541).—Thermal bromination of C_3H_8 is a chain reaction since it is decelerated by air, has an induction period, and the rate is altered by a change in the ratio of vol. to surface. The primary reaction is dissociation of Br followed by $C_3H_8 + Br \rightarrow C_3H_7 + HBr$, $C_3H_7 + Br_2 \rightarrow PrBr + Br$, $C_3H_8 + Br \rightarrow C_3H_7 + HBr$. . . Under all circumstances very large amounts of $Pr^{\beta}Br$ are produced probably by the reactions, $Pr^{\alpha}Br \rightleftharpoons CHMe:CH_2 + HBr \rightleftharpoons Pr^{\beta}Br$. The formation of $CH_2(CH_2Br)_2$ and CMe_2Br_2 is probably due to further direct substitution whereas $CH_2Br \cdot CHMeBr$ probably arises by addition of Br to $CHMe:CH_2$. Higher and unsaturated bromides are also produced. Increase in temp. increases the proportion of $Pr^{\alpha}Br$ but only slightly augments the amount of polybromides. Unsaturated compounds are markedly increased, particularly with high [Br]. Formation of polybrominated propanes increases greatly with [Br]; this has little influence on the unsaturated compounds, formation of which is mainly a function of temp., and scarcely affects the ratio of $Pr^{\alpha}Br$ to $Pr^{\beta}Br$. With diminishing time of reaction the relative amounts of polybromides and unsaturated compounds are diminished. The bromides of Fe, Cu, Tl, or Zn on pumice favour the production of greater or smaller amounts of polybromide probably by accelerating the decomp. of $Pr^{\alpha}Br$ into $CHMe:CH_2$. The formation of unsaturated bromides is not greatly influenced by

the catalysts which favour the production of tri- and tetra-bromides. H. W.

isoButane from normal butane.—See B., 1940, 343.

Catalytic alkylation of isobutane with gaseous olefines.—See B., 1940, 341.

Catalytic polymerisation of olefines.—See B., 1940, 343.

Separation of the isomeric hexenes by batch fractionation. A. ROSE (J. Amer. Chem. Soc., 1940, 62, 793—795).—400 theoretical plates are required for sharp fractionation of isomeric hexenes of similar b.p. R. S. C.

Attempted separation of isomeric hexenes by fractional distillation. F. C. WHITMORE, M. R. FENSKE, D. QUIGGLE, H. BERNSTEIN, T. P. CARNEY, S. LAWROSKI, A. H. POPKIN, R. B. WAGNER, W. R. WHEELER, and J. S. WHITAKER (J. Amer. Chem. Soc., 1940, 62, 795—800).—The Podbielniak-Simons-Taylor column has an efficiency of ~15 theoretical plates and is ineffective for separation of hexene mixtures with b.p. ranges 1.5° or 2.7° (cf. Rose, preceding abstract). The work of Goldwasser *et al.* (A., 1939, I, 478, 479; II, 401) is erroneous. R. S. C.

Hydrogenation of octenes.—See B., 1940, 343.

Formation of $\alpha\beta$ -dichloroethane from ethylene and hypochlorous acid.—See A., 1940, I, 260.

Preparation of *as*-tetrachlorodifluoroethane. W. T. MILLER (J. Amer. Chem. Soc., 1940, 62, 993).— $CCl_2F \cdot CClF_2$ and $AlCl_3$ at 100° (5 hr.) give $CCl_3 \cdot CClF_2$ and small amounts of C_2Cl_6 (more on longer heating). R. S. C.

Removal of substituents from vinyl polymerides. F. T. WALL (J. Amer. Chem. Soc., 1940, 62, 803—806).—The fraction of Cl remaining in mixed vinyl chloride-vinyl acetate polymerides after treatment with Zn can be predicted using formulæ which are derived by statistical methods. W. R. A.

Nitration of ethane.—See B., 1940, 341.

Synthesis of isopropyl alcohol from propylene. I—III. M. KATUNO (J. Soc. Chem. Ind. Japan, 1940, 43, 5—8B, 8—11B, 11—14B).—I. $Pr^{\beta}HSO_4$ is rapidly hydrolysed in H_2SO_4 without formation of Pr^{β}_2O or C_3H_6 if the concn. of acid is >40%; the $Pr^{\beta}OH$ is quantitatively obtained by distillation if the amount of H_2O used is that required for hydrolysis and formation of the azeotropic mixture. Absorption of C_3H_6 is best effected by 87% H_2SO_4 , but is improved by use of 68% acid and a little Ag_2SO_4 , which accelerates absorption.

II. Apparatus for the reactions $2\text{C}_3\text{H}_6 + \text{H}_2\text{SO}_4 \rightarrow \text{Pr}^{\beta}\text{SO}_4 \rightarrow 2\text{Pr}^{\beta}\text{OH} + \text{H}_2\text{SO}_4$ is described. The reaction mechanism is discussed.

III. Hydrolysis of $\text{Pr}^{\beta}\text{SO}_4$ is investigated. Formation of $\text{Pr}^{\beta}\text{HSO}_4$ is rapid in H_2O , but further hydrolysis to $\text{Pr}^{\beta}\text{OH}$ requires H^+ or OH^- .

R. S. C.

Physical constants of pentan- γ -ol. F. C. WHITMORE and J. D. SURMATS (J. Amer. Chem. Soc., 1940, **62**, 995).— EtCHO (prepared from $\text{Pr}^{\alpha}\text{OH}$ by Cu-dehydrogenation), b.p. $48.0^\circ/736$ mm., and $\text{MgEtCl-Et}_2\text{O}$ give 60% of CHEt_2OH , b.p. $114.4^\circ/740$ mm. Commercial (Sharples) CHEt_2OH yielded 27% of the pure alcohol.

R. S. C.

Electrochemical oxidation of *n*-hexanol. W. R. LOWSTUTER and A. LOWY (Trans. Electrochem. Soc., 1939, **77**, Preprint 21, 263–270).— $n\text{-C}_6\text{H}_{13}\text{OH}$ (I), oxidised electrochemically, yields $n\text{-C}_5\text{H}_{11}\text{CO}_2\text{H}$ (II), $n\text{-C}_5\text{H}_{11}\text{CO}_2\text{C}_6\text{H}_{13}$, and small amounts of CO_2 , CO , and a residue of high b.p. Max. current efficiency of 59.9%, calc. only as oxidation to (II), is obtained with an electrolytically prepared PbO_2 anode in 9% (I) in 5% H_2SO_4 at 12° , using a c.d. of 1.1 amp. per sq. dm.

D. F. R.

Preparation of unsaturated higher alcohols. IV. S. KOMORI (J. Soc. Chem. Ind. Japan, 1940, **43**, 34–35B; cf. A., 1939, II, 491).—Hydrogenation of unsaturated esters to unsaturated higher alcohols is well effected in presence of Cd chromite at 335° . X-Ray diagrams show that the catalyst does not contain CdO or Cr_2O_3 . Co chromite may also be used, but Cd vanadate, tungstate, or molybdate is less satisfactory.

R. S. C.

Phenolic sugar alcohols.—See B., 1940, 343.

Keten acetals. IV. Polymerides of keten diethyl acetal. P. R. JOHNSON, H. M. BARNES, and S. M. McELVAIN (J. Amer. Chem. Soc., 1940, **62**, 964–972; cf. A., 1938, II, 427).— $\text{CH}_2\text{C}(\text{OEt})_2$ (I) is stable in new Pyrex glass at $190\text{--}240^\circ$ (6 hr.), in new soft glass in diffuse light at room temp., or in old glass washed with aq. alkali or in presence of KOBU^r . Polymerisation occurs in acid-washed glass. Bz_2O_2 is without effect, but the following relative efficiency of catalysis is reported: $\text{AlCl}_3 > \text{FeCl}_3 > \text{ZnCl}_2 > \text{CdCl}_2 > \text{CoCl}_2 > \text{NiCl}_2 > \text{BaCl}_2, \text{HgCl}_2, \text{CaCl}_2$, the stability of the polymerides varying. CdCl_2 (0.06%) gives a wax, containing 45% of (I) and a white, solid polymeride (II), stable at 200° and to boiling 10% NaOH . Dil. acid at room temp. converts (II) into a red oil; boiling dil. acid gives a reddish-black glass (III) and CO_2 . Little EtOH is lost in formation of (II), but more is lost during acid hydrolysis. (III) is sol. in, but unchanged by, aq. alkali. The amount of CO_2 evolved, analysis of (III), and KMnO_4 oxidation of (III) to CO_2 (80%) and AcOH indicate that (II) is about $(\text{OEt})_2\text{CMe}[\text{CH}_2\text{C}(\text{OEt})_2]_{21}\text{CH}_2\text{C}(\text{OEt})_3$ and (III) about $\text{COMe}[\text{CH}:\text{C}(\text{OH})]_{21}\text{Me}$. The insolubility indicates cross-linking (intermol. loss of EtOH) in (II), but this cannot be extensive owing to the high OEt content. 10% H_2SO_4 and (III) at 200° give only traces of COMe_2 and AcOH but 5% NaOH gives larger amounts thereof and a reddish-black substance (IV) (structure proposed), which on repeated hydrogenation (Raney Ni; $225^\circ/200$ atm.; 1% NaOH)

gives a colourless solid (12%) with EtOH , AcOH , and a red oil. Polymerisation of (I) by 0.36% of CdCl_2 is exothermic and gives 13% of unstable dimeride, b.p. $61\text{--}62^\circ/0.5$ mm., probably

$(\text{OEt})_2\text{CMe}:\text{CH}:\text{C}(\text{OEt})_2$ (with 5% H_2SO_4 gives COMe_2 and with HCl-EtOH gives $\text{CH}_2\text{Ac}:\text{CO}_2\text{Et}$), 20% of a trimeride (V), $\text{CMe}(\text{OEt})_3$, EtOH , and a solid similar to (II). (V) may be

$(\text{OEt})_2\text{CMe}:\text{CH}_2:\text{C}(\text{OEt})_2:\text{CH}:\text{C}(\text{OEt})_2$, but is isolated after distillation as (?) 1:1:3:3:5:5-hexaethoxycyclohexane (VI), b.p. $91\text{--}92^\circ/0.1$ mm., with some EtOH . With 5% H_2SO_4 , (VI) gives a little $s\text{-C}_6\text{H}_3(\text{OEt})_3$ [not formed from (V)]. A trace of acid in boiling 95% EtOH converts (VI) into

$\text{CH}_2\text{Ac}:\text{CO}:\text{CH}_2:\text{CO}_2\text{Et}$. Absence of head-to-head polymerisation is confirmed by absence of $(\text{CH}_2:\text{CO}_2\text{H})_2$ when (IV) is oxidised with HNO_3 and is due to the strength of the anionoid centre in (I). $\text{CHHal}:\text{C}(\text{OEt})_2$ and $\text{CHAl}_2:\text{C}(\text{OEt})_2$ are stable to light, CdCl_2 , and Bz_2O_2 . BF_3 or $\text{BF}_3\text{Et}_2\text{O}$ converts $\text{CHHal}:\text{C}(\text{OEt})_2$ slowly into a red oil.

R. S. C.

Kinetics of decarboxylation in solution.—See A., 1940, I, 260.

Mechanism of polymerisation of vinyl acetate and methyl vinyl ketone.—See A., 1940, I, 263.

Chlorinations with sulphuryl chloride. III.

(a) Peroxide-catalysed chlorination of aliphatic acids and acid chlorides. (b) Photochemical sulphonation of aliphatic acids. M. S. KHARASCH and H. C. BROWN (J. Amer. Chem. Soc., 1940, **62**, 925–929; cf. A., 1940, II, 72).—In absence of catalysts and in the dark, boiling aliphatic acids and acid chlorides do not react with SO_2Cl_2 . In presence of peroxides (Bz_2O_2) chlorination occurs nearly quantitatively (except for AcOH or AcCl), preferentially at a C remote from the CO. Dilution with CCl_4 is advisable for the acids. Thus EtCO_2H gives $\text{Cl}[\text{CH}_2]_2\text{CO}_2\text{H}$ (55%) and $\text{CHMeCl}:\text{CO}_2\text{H}$ (45%). EtCOCl gives $\text{Cl}[\text{CH}_2]_2\text{COCl}$ (60%) and $\text{CHMeCl}:\text{COCl}$ (40%). $\text{Pr}^{\beta}\text{CO}_2\text{H}$ gives $\text{CH}_2\text{Cl}:\text{CHMe}:\text{CO}_2\text{H}$ (85%) and $\text{CMe}_2\text{Cl}:\text{CO}_2\text{H}$ (15%). $\text{Pr}^{\beta}\text{COCl}$ gives $\text{CH}_2\text{Cl}:\text{CHMe}:\text{COCl}$ (80%) and $\text{CMe}_2\text{Cl}:\text{COCl}$ (20%). $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ gives $\text{Cl}[\text{CH}_2]_3\text{CO}_2\text{H}$ (45%), $\text{CHMeCl}:\text{CH}_2:\text{CO}_2\text{H}$ (45%), and $\text{CHEtCl}:\text{CO}_2\text{H}$ (10%). $\text{Pr}^{\alpha}\text{COCl}$ gives $\text{Cl}[\text{CH}_2]_3\text{COCl}$ (30%), $\text{CHMeCl}:\text{CH}_2:\text{COCl}$ (55%), and $\text{CHEtCl}:\text{COCl}$ (15%). $\text{Bu}^r\text{CO}_2\text{H}$ gives $\beta\text{-chloro-}\alpha\text{-dimethylpropionic acid}$, m.p. $40\text{--}42^\circ$, b.p. $126\text{--}129^\circ/30$ mm. (amide, m.p. $108\text{--}109^\circ$), and Bu^rCOCl gives the corresponding chloride, b.p. $85\text{--}86^\circ/60$ mm. AcOH gives $>50\%$ of $\text{CH}_2\text{Cl}:\text{CO}_2\text{H}$, but AcCl does not react even in boiling PhCl . I catalyses reaction of EtCOCl at 70° , but only $\text{CHMeCl}:\text{COCl}$, formed by dissociation of SO_2Cl_2 into SO_2 and Cl_2 , is obtained. In light and absence of catalysts sulphonation occurs, mainly at $\text{C}_{(8)}$. Boiling EtCO_2H and SO_2Cl_2 , when irradiated, give 37% of $\text{SO}_3\text{H}[\text{CH}_2]_2\text{CO}_2\text{H}$, + $0.5\text{H}_2\text{O}$ (or more) (Ba salt, + $5\text{H}_2\text{O}$; anhydride, m.p. $76\text{--}77^\circ$); $\text{Pr}^{\alpha}\text{CO}_2\text{H}$ and $\text{Bu}^{\beta}\text{CO}_2\text{H}$ are also sulphonated (no details), but AcOH does not react. Sulphonation of cyclohexane by SO_2Cl_2 in light is catalysed (5% yield) by AcOH .

R. S. C.

Purification of fatty esters of high mol. wt. L. O. BUXTON and R. KAPP (J. Amer. Chem. Soc.,

1940, 62, 986).—These esters are purified by dissolution in $(\text{CH}_2\text{Cl})_2$, neutralisation by 38% KOH (amount determined by titration), filtration, and distillation.

R. S. C.

Hydrolysis of fats and fatty acid esters.—See A., 1940, I, 260.

Mechanism of pyrolysis of castor oil. S. ISHIKAWA, T. TOSIMITSU, A. MIYATA, J. ARAKI, and R. SOMENO (Sci. Rep. Tokyo Bunrika Daigaku, 1939, 3, 273—285).—Pyrolysis of castor oil (I) in presence of SiO_2 or sea-sand (better than borax-pumice) at 480—500° gives $n\text{-C}_6\text{H}_{13}\cdot\text{CHO}$ and $\text{CH}_2\text{:CH}[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$ (II) with small amounts of $n\text{-C}_6\text{H}_{13}\cdot\text{CH:C}(\text{C}_6\text{H}_{11}\cdot n)\cdot\text{CHO}$ (2:4-dinitrophenylhydrazones, m.p. 128°), the corresponding alcohol, $n\text{-C}_6\text{H}_{13}\cdot\text{CO}_2\text{H}$, and $n\text{-C}_7\text{H}_{15}\cdot\text{OH}$. Addition of metal oxides, except possibly Mo_2O_5 , to the SiO_2 does not improve the yield. The structure of (II) is confirmed by oxidation with KMnO_4 and O_3 . (II) does not rearrange to $\text{CHMe}\cdot\text{CH}[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$. Citronellal at 420° gives only a little $\Delta^3\cdot^8\text{-p-menthadiene}$ and $l\text{-menthol}$ gives only a little $\Delta^3\text{-p-menthene}$. Oleic acid gives no aldehyde. Pyrolysis of (I) follows conjugation of the OH with C:C .

R. S. C.

Fatty acids. V. Preparation of methyl ricinoleate and ricinoleic acid by fractional crystallisation. J. B. BROWN and N. D. GREEN (J. Amer. Chem. Soc., 1940, 62, 738—740; cf. A., 1939, II, 4).—Crystallisation of Me ricinoleate (prep. from castor oil described) from COMe_2 at $\sim -50^\circ$ gives a 99.5%-pure ester, m.p. -4° or -4.5° , $[\alpha]_D^{25} +7.41^\circ$ or $[\alpha]_D^{25} +5.19^\circ$ in COMe_2 . Hydrolysis and subsequent low-temp. crystallisation gives a 95.6%-pure acid, m.p. 5.5° , $[\alpha]_D^{25} +7.15^\circ$ in COMe_2 .

R. S. C.

Chlorinated oils. T. MATSUMOTO and S. IWAI (J. Soc. Chem. Ind. Japan, 1940, 43, 16—18B).—Addition of Cl_2 to linseed, sardine, or olive oil in CCl_4 occurs mainly at one ethylenic linking. Some evolution of HCl occurs and in this decomp. colloid formation, evidenced by increase in η , occurs.

R. S. C.

Structure of pantothenic acid. R. J. WILLIAMS and R. T. MAJOR (Science, 1940, 91, 246).—The cryst. lactone, $\text{C}_6\text{H}_{10}\text{O}_3$, m.p. 91—92° (from Ba pantothenate concentrates), is α -hydroxy- $\beta\beta$ -dimethyl- γ -butyrolactone. Condensation with β -alanine gives physiologically-active pantothenic acid. L. S. T.

Calythron. A. R. PENFOLD and J. L. SIMONSEN (J.C.S., 1940, 412—415).—The essential oil from *Calythrix tetragona* when extracted with aq. NaOH gives the Na salt, m.p. $(+\text{xH}_2\text{O})$ 110—111° (anhyd.)

196°, of calythrone (I), $\text{CO} \begin{smallmatrix} \text{CMe}\cdot\text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH}\cdot\text{COBu}^\beta$, b.p. 142°/14 mm. (Cu derivative, m.p. 208—210°), which is oxidised by aq. NaOH—NaOBr to CHBr_3 , $\text{Bu}^\beta\text{CO}_2\text{H}$, dimethylmaleic anhydride (II), and a Br_2 -acid, probably $\text{CHBr}_2\cdot\text{CO}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$, m.p. 129°. (I) has β -diketonic properties, due to the opening of the lactone ring; its dioxime anhydride, m.p. 135°, is considered to be $\text{CO} \begin{smallmatrix} \text{CMe}\cdot\text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH}\cdot\text{COBu}^\beta$. (II)

has pseudoketonic properties, giving a semicarbazone, m.p. 238° (when rapidly heated, 248°), and a p-

nitro-, m.p. 214°, and a 2:4-dinitro-phenylhydrazones, decomp. 253—255°. These are sol. in aq. Na_2CO_3 , and are therefore $\text{CMe}\cdot\text{CMe} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O} \text{C:N}R$, rather than

$\text{CMe}\cdot\text{CMe} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR} \text{CO}$. (II) is reduced catalytically to meso- and by Clemmensen reagent to *dl-s*-dimethylsuccinic acid, and is oxidised to AcCO_2H . With $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ and aq. KOH, followed by MeOH, (I) gives *p*-phenylphenacyl Me dimethylmaleate, m.p. 95°.

E. W. W.

Long-chain acids. II. Aleuritic acid. P. C. MITTER and P. C. DUTTA (J. Indian Chem. Soc., 1939, 16, 673—676).— $\text{OPh}[\text{CH}_2]_5\cdot\text{Br}$ and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (2 mol.) with Na—EtOH give Et ω -phenoxy-pentamethyleneacetoacetate, b.p. 180°/3 mm., which with Na—Et₂O and $\text{COCl}[\text{CH}_2]_8\cdot\text{CO}_2\text{Et}$ affords after hydrolysis (EtOH—KOH) *o*-phenoxy-*i*-ketopalmitic acid, m.p. 89° (Et ester, b.p. 252°/2 mm., m.p. 50°). This with HBr—AcOH gives *o*-bromo-*i*-ketopalmitic acid, m.p. 69°, in poor yield, which with AcOH—KOAc, followed by esterification (EtOH—HCl), yields Et *o*-acetoxy-*i*-ketopalmitate, b.p. 219—220°/3 mm., m.p. 54—55°, which could not be satisfactorily reduced.

F. R. S.

Dialkyl adipates. R. A. FEAGAN, jun., and J. E. COPENHAVER (J. Amer. Chem. Soc., 1940, 62, 869—870).—The following are prepared from ROH and the acid at 150—155° or acid chloride at slightly > room temp.: *di-n-amy*l, m.p. -14° , *-hexyl*, m.p. -9° to -7° , *-heptyl*, m.p. 3.8—4.5°, *-octyl*, m.p. 9.5—9.8°, *-nonyl*, m.p. 21.6° (lit. 17—18.5°), *-decyl*, m.p. 27.4°, *-undecyl*, m.p. 34.7°, *-dodecyl*, m.p. 39.3°, *-tridecyl*, m.p. 45.9°, *-tetradecyl*, m.p. 49.4°, *-pentadecyl*, m.p. 55°, *-hexadecyl*, m.p. 57.3° (lit. 53°), *-heptadecyl*, m.p. 61.8°, *-octadecyl*, m.p. 63.4°, *-nonadecyl*, m.p. 66.7°, and *-eicosyl*, m.p. 65.2°, adipate. There is only slight alternation in m.p., which are corr.

R. S. C.

Polarimetric study of action of heat on crystalline *l*-malic acid. R. DESCAMPS (Bull. Soc. chim. Belg., 1940, 49, 1—20).— $[\alpha]$ of specimens of cryst. *l*-malic acid (I) heated at 85° to 120° increases with the time of heating, the curves being usually S-shaped and tending to an upper limit for temp. $<100^\circ$, whilst those for temp. $>100^\circ$ show a max. The rotatory dispersion ($\lambda\lambda$ 5893—4358), which is anomalous in solutions of the unchanged substance, becomes less so as the heating proceeds. The products, as in the case of aq. solutions (cf. A., 1939, II, 468), are fumaric acid and one or more optically active dehydration products. Here also the Darbais rule is applicable.

F. L. U.

Optical activity and chemical structure in tartaric acid. X. Influence of substituent and solvent effect. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1940, 15, 55—59).—Data on $[M]_D^{25}$ for compounds $\text{CHR} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH}\cdot\text{CO}_2\text{Et}$ (A) in C_6H_6 , EtOH, and cyclohexane (I) are given. The $[\alpha]$ decreases as the parachor of R increases, in accordance with the rule found (A., 1939, I, 357) for compounds A with $\text{CR}'\text{R}''$ for CHR, and the sequence of solvent effects is also the same, viz., $\text{C}_6\text{H}_6 > \text{EtOH} > (\text{I})$.

The following are described: *Et*₂ *d*-butylidenedioxy-succinate (R = Pr^a), b.p. 160°/15 mm., $[\alpha]_D^{20}$ -55.80°; *Et*₂ *d*-isobutylidenedioxy-succinate (R = Pr^b), b.p. 160°/20 mm., $[\alpha]_D^{20}$ -54.17°; *Et*₂ *d*-heptylidenedioxy-succinate, b.p. 190°/16 mm., $[\alpha]_D^{20}$ -41.76°. Vals. of $[\alpha]_D^{20}$ in C₆H₆, EtOH, and (I) are also recorded.

F. J. G.

Improved preparation of *DL*-threonic and -erythronic acids. J. W. E. GLATTFELD and E. RIETZ (J. Amer. Chem. Soc., 1940, **62**, 974—977).—CH₂:CH·CH₂:CN and Br in Bu^oOH and light petroleum give the dibromide, converted by NaOEt—EtOH into CH₂Br·CH:CH·CN (55%), b.p. 80—85°/12 mm. The dibromide, prepared from CH₂:CH·CH₂:CO₂Et (I) by Br in Bu^oOH, with NaOEt at 0° gives 60% of CH₂Br·CH:CH·CO₂Et (II). CH₂Cl·CH:CH·CO₂Et, similarly prepared in 65% yield, is hydrolysed and oxidised (OsO₄—BaClO₃) to *DL*-threonic acid (59%). At <35° (I) similarly gives β-hydroxybutyrolactone (35%), which with P₂O₅ in dioxan gives isocrotonolactone (53%) and thence *DL*-erythronolactone (45%).

R. S. C.

Preparation of alkali bismuth saccharates. G. O. DOAK (J. Amer. Pharm. Assoc., 1940, **29**, 108—111).—The following were prepared by interaction of Bi(OH)₃ with saccharic acid and the appropriate alkali in H₂O: *K*₂ di- (I), *Na* di-, *Na K* di- and *K*₂ tri-bismuthylsaccharate. (I) with 10% HCl affords dibismuthylsaccharic acid. (I) is more stable in H₂O or serum than the corresponding tartrate or gluconate.

F. O. H.

Manufacture of formaldehyde.—See B., 1940, 343.

Aldehydic perfumes. III. Synthesis of β-hydroxynonaldehyde. S. ISHIKAWA and T. SAKURAI (Sci. Rep. Tokyo Bunrika Daigaku, 1939, **3**, 287—289; cf. A., 1939, II, 406).—The aldehyde [2:4-dinitrophenylhydrazone, m.p. 124.6° (corr.)] is prepared from castor oil by oxidation by KMnO₄ to 6*κ*-trihydroxystearic acid, m.p. 122—123°, and thence by Pb₃O₄—Ac₂O—AcOH.

R. S. C.

Biochemical preparation of aliphatic ketones.—See A., 1940, III, 540.

Thermal decomposition of diacetyl.—See A., 1940, I, 259.

Reducing powers of various sugars with alkaline copper citrate reagent. H. S. ISBELL, W. W. PIGMAN, and H. L. FRUSH (J. Res. Nat. Bur. Stand., 1940, **24**, 241—246).—Scales' method (A., 1919, ii, 435), modified by increasing the time of boiling to 6 min., is convenient for determining reducing sugars. Sugars with OH at C₁₃ *trans* to OH at C₁₄ and C₁₅ have the highest reducing power, whilst those with OH at C₁₃ or C₁₄ in the *cis* position have a lower reducing power. The configuration of OH at C₁₂ does not greatly affect the reducing power. When the glycosidic linkage of a disaccharide is at C₁₃ the mol. reducing power is < that of the corresponding monosaccharide, but if the linking is at C₁₄ or C₁₅ the reducing power is slightly > that of the monosaccharide. Under the conditions used the presence of BaBr₂ (6.5%) decreases the reducing val. by ~4%.

J. W. S.

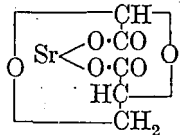
α- and β-Methyl lyxosides, mannosides, gulosides, and heptosides of like configuration. H. S. ISBELL and H. L. FRUSH (J. Res. Nat. Bur. Stand., 1940, **24**, 125—151; cf. A., 1937, II, 177).—*d*-Lyxose refluxed with HCl—MeOH affords α-methyl- (I), m.p. 108° (cf. Phelps *et al.*, A., 1926, 501) [CaCl₂ compound (+2H₂O), $[\alpha]_D^{20}$ +31.3° in H₂O], and β-methyl-*d*-lyxopyranoside, m.p. 118°, $[\alpha]_D^{20}$ -128.1° in H₂O (triacetate, m.p. 88—89°, $[\alpha]_D^{20}$ -109.5° in CHCl₃); the latter and HIO₄ give a substance, $[\alpha]_D^{20}$ -125.5° [cf. product from (I), Maclay *et al.*, A., 1938, II, 430]. β-Methyl-*d*-mannopyranoside tetra-acetate and Ba(OMe)₂—MeOH, followed by Pr^oOH, yield β-methyl-*d*-mannopyranoside Pr^o alcoholate, m.p. 74—75°, $[\alpha]_D^{20}$ -53.3° in H₂O, stable in presence of Pr^oOH vapour; Pr^oOH is lost at 105° in vac.; 70% of the Pr^oOH is lost at 77° in O₂. α-Methyl-*d*-α-galaheptopyranoside is prepared, identical with the compound named as the β-form (cf. Hann *et al.*, A., 1936, 193); nomenclatures are discussed. *d*-α-Galaheptose hydrate and Me₂SO₄—NaOH, then Ac₂O, give β-methyl-*d*-α-galaheptopyranoside penta-acetate, m.p. 171—173°, $[\alpha]_D^{20}$ +77.6° in CHCl₃, converted by Ba(OMe)₂—MeOH into β-methyl-*d*-α-galaheptopyranoside. *d*-α-Glucoheptose and HCl—MeOH give β- (CaCl₂ compound, +2H₂O, $[\alpha]_D^{20}$ -56.1° in H₂O) and α-methyl-*d*-α-glucoheptopyranoside, m.p. 106—107°, $[\alpha]_D^{20}$ +111.5° in H₂O (penta-acetate, m.p. 174—175°, $[\alpha]_D^{20}$ +107.4° in CHCl₃; cf. product, m.p. 169°, of Haworth *et al.*, A., 1932, 46), the latter being isolated by decomp. of its CaCl₂ compound (+H₂O), $[\alpha]_D^{20}$ +69.1° in H₂O. *d*-β-Galaheptose and HCl—MeOH give α-methyl-*d*-β-galaheptopyranoside, m.p. 154—155°, $[\alpha]_D^{20}$ -108° in H₂O (cf. Hann *et al.*, A., 1937, II, 178). Photomicrographs of the new glycosides are shown. The configurations of all asymmetric C in the pyranose ring affect the rate of hydrolysis. There is no fixed relationship between the configuration of the glycosidic C and the relative rates for hydrolysis of the α- and β-modifications. Aldopyranosides having *trans*-configurations for C₁₁ and C₁₃ are hydrolysed more slowly than the corresponding *cis*-forms. Mol. rotations of the methylglycopyranosides are compared and there is support for classifying the methyl-lyxopyranosides in the *d*-mannose rather than the *l*-gulose series.

A. T. P.

Use of the benzyl radical in syntheses of methylated sugars. I. 4:6-Dimethylglucose. D. J. BELL and J. LORBER (J.C.S., 1940, 453—455).—The prep. of 4:6-dimethylglucose (I) (A., 1937, II, 484) is easily effected by converting the 2:3-diacetate of 4:6-benzylidene-α-methylglucoside (II) (Mathers *et al.*, A., 1933, 938) by KOH and CH₂PhCl in xylene at 95—100° into the 2:3-(CH₂Ph)₂ derivative (III), m.p. 93°, $[\alpha]_D^{20}$ -31.2° (all rotations in CHCl₃), of (II). Aq. HCl in boiling COMe₂ hydrolyses (III) to 2:3-dibenzyl-α-methylglucoside, m.p. 75—76°, $[\alpha]_D^{20}$ +18.8°. When methylated by Purdie's reagents, either directly or after treatment with Me₂SO₄—NaOH in COMe₂, this gives 2:3-dibenzyl-4:6-dimethyl-α-methylglucoside, b.p. 215—220° (bath)/0.03 mm., $[\alpha]_D^{20}$ +32.9°, which is debenzylated by Na in EtOH to 4:6-dimethyl-α-methylglucoside, b.p. 160° (bath)/0.5 mm. This [which with *p*-C₆H₄Me·SO₂Cl in C₅H₅N

gives its 2:3-di-*p*-toluenesulphonate, new m.p. 113° (cf. Mather *et al.*, A., 1933, 1037)] is hydrolysed by *N*-HCl at 100° to (I). E. W. W.

Cleavage of the carbon chain of β -glucosan by periodic acid. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1940, 62, 958—961).— β -Glucosan (I) consumes 2 HIO₄, giving HCO₂H (1 mol.) and *L*'-oxy-*D*-methylenediglycollic dialdehyde, $[M]_D -15.0^\circ$, oxidised by Br-SrCO₃ to *Sr L*'-oxy-*D*-methylenediglycolate (II) (45%), +5H₂O, +H₂O, $[\alpha]_D^{20} +36.9^\circ$ in H₂O, and anhyd., with smaller amounts of SrC₂O₄ and *Sr D*-glycerate. The



(II.)

accepted structure of (I) is thus confirmed. (I) is stable to 2.5*N*-HCl. R. S. C.

Glucofuranosides and thioglucofuranosides. VII. Crystalline alkylfuranosides and dimethyl acetal of *d*-mannose. A. SCATTERGOOD and E. PACSU (J. Amer. Chem. Soc., 1940, 62, 903—910; cf. A., 1939, II, 407).—60% of α -methyl-*d*-mannofuranoside (I) is obtained from mannose Et₂ mercaptal (II) by HgCl₂-MeOH, Hg being a permissible reagent for removal of excess of HgCl₂ in this and other cases. In this and other preps. of (I) the mother-liquors contain β -methyl-*d*-mannofuranoside (III), m.p. 47°, $[\alpha]_D^{20} -12.6^\circ$ in H₂O, isolated as CaCl₂ compound, +3H₂O, $[\alpha]_D^{20} -58.5^\circ$ in H₂O, and recovered therefrom by Ag₂C₂O₄. CaCl₂ influences the α of (III). The tetra-acetate, m.p. 61—62°, of (I) has $[\alpha]_D^{20} -108.8^\circ$ in CHCl₃, +120.3° in *cis*- and +105.3° in *trans*-(CHCl₃)₂. The mercaptal method gives also α -ethyl-, m.p. 90°, $[\alpha]_D^{20} +105.0^\circ$, α -*n*-, m.p. 96°, $[\alpha]_D^{20} +96.0^\circ$, and α -iso-propyl-*d*-mannofuranoside, m.p. 96.7°, $[\alpha]_D^{20} +96.7^\circ$ (all in H₂O). The penta-acetate of (II) with HgCl₂-MeOH gives a penta-acetate, hydrolysed by NaOMe-MeOH to mannose Me₂ acetal, m.p. 101°, $[\alpha]_D^{20} +0.6^\circ$ in H₂O, stable in H₂O or alkali but converted in 0.05% HCl first into (I) and (III) (*k* 0.024) and then into *d*-mannose (*k* 0.00118). Introduction of the *F* term (A., 1940, II, 6) (= -4475) accounts for the $[M]$ of the mannose derivatives. Fischer-Hirschfelder models are used to prove the contention (*loc. cit.*) that only one *cis*- and one *trans*-form of aldohexopyranoses are possible; the *cis*-form is unstable by repulsion. *F* must be due to the orientation about the C-O linkings of all the OH, probably owing to H linkings. R. S. C.

Monothioacetals of galactose. M. L. WOLFROM and D. I. WEISBLAT (J. Amer. Chem. Soc., 1940, 62, 878—880).—*d*-Galactose Et₂ mercaptal penta-acetate and POCl₃ in boiling AcCl give aldehydo-1-chloro-1-ethylthiol-*d*-galactose penta-acetate, m.p. 111—113°, $[\alpha]_D^{22} -27^\circ$ in CHCl₃, unstable, which with CaSO₄ and Ag₂CO₃ in MeOH or EtOH gives *d*-galactose Me₂, m.p. 119—120°, $[\alpha]_D^{22} +42.5^\circ$ in CHCl₃, and Et₂ monothioacetal penta-acetate, m.p. 104—105°, $[\alpha]_D^{22} +50^\circ$ in CHCl₃, hydrolysed by cold NaOMe-MeOH to *d*-galactose Me₂, m.p. 146—147°, $[\alpha]_D^{22} +50^\circ$ in H₂O, and Et₂ monothioacetal, m.p. 155—156°, $[\alpha]_D^{22} +53^\circ$ in H₂O, respectively, stable to hot Fehling's solution unless previously hydrolysed by acid (gives RSH). N** (A., II.)

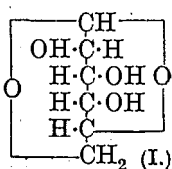
d-Galactose Me₂ acetal penta-acetate and AcCl at 0° give aldehydo-1-chloro-1-methoxy-*d*-galactose penta-acetate, m.p. 155—156°, $[\alpha]_D^{22} -38^\circ \rightarrow +15^\circ$ in 24 hr. in CHCl₃, $-53^\circ \rightarrow -42.5^\circ$ in 10 hr. in C₆H₆.

R. S. C.

Walden inversion in the altrose series. G. J. ROBERTSON and W. WHITEHEAD (J.C.S., 1940, 319—323).—4:6-Benzylidene-2:3-anhydro- α -methylaltroside (I) with boiling aq. KOH gives 4:6-benzylidene- α -methylaltroside (II) (cf. A., 1935, 1225), which with *p*-C₆H₄Me-SO₂Cl-C₅H₅N gives its 2:3-di-*p*-toluenesulphonate (III), m.p. 170—175°, $[\alpha]_D^{15} +46.9^\circ$ in CHCl₃. With NaOMe-MeOH, this gives a quant. yield of 4:6-benzylidene-2:3-anhydro- α -methylmannoside (IV), identical with that obtained from 4:6-benzylidene- α -methylglucoside 2-*p*-toluenesulphonate (V) (*loc. cit.*). Thus hydrolysis of (III), like that of (V), involves Walden inversion at C₃. Hydrolysis of (IV) by aq. KOH gives a quant. yield of (II). 50% Aq. N₂H₄.H₂O at 110—120° opens the (CH₂)₂O rings of (IV) and of (I) in 12 and 30 hr., respectively. The product from (IV) is 4:6-benzylidene-3-hydrazino- α -methylaltroside, m.p. 196°, $[\alpha]_D^{15} +53.7^\circ$ in C₅H₅N, since with conc. HCl at room temp. it gives pyrazolyl-5- α -glycerol hydrochloride. The isomeride, from (I), is therefore 4:6-benzylidene-2-hydrazino- α -methylaltroside, m.p. 144°, $[\alpha]_D^{15} +67.96^\circ$ in CHCl₃. The 3:6-anhydro-ring in altrose is formed from 2-methyl- α -methylaltroside 3-*p*-toluenesulphonate (VI), m.p. 118°, $[\alpha]_D^{15} +88.1^\circ$ in CHCl₃, obtained by hydrolysing its 2:3-CHPh₂ derivative (*loc. cit.*) by dil. HCl in COMe₂ on the water-bath to const. rotation. The 4:6-Bz₂ derivative, m.p. 113°, $[\alpha]_D^{10} +94.69^\circ$ in CHCl₃, of (VI) is hydrolysed by boiling MeOH-NaOMe to a dark product which after acidification gives 2-methyl-3:6-anhydro- α -methylaltroside (VII), m.p. 107—108°, $[\alpha]_D^{14} +105.1^\circ$ in CHCl₃. Under milder conditions, *e.g.*, at room temp., (VI) only is obtained. Under no conditions is the theoretically possible 3:4-anhydro-compound obtained. With 2*N*-KOH at 100°, or 10% NaOMe-MeOH, (VII) is stable; with boiling 5% HCl, (VII) gives, with decomp., 2-methyl-3:6-anhydroaltrose, a syrup, $[\alpha]_D^{10} +81.27^\circ$ in CHCl₃, +106.3° in H₂O. Methylation of (VII) by the Purdie reagents gives the fully methylated 2:4-dimethyl-3:6-anhydro- α -methylaltroside, a syrup, $[\alpha]_D^{15} +69.04^\circ$ in CHCl₃. A further unsuccessful attempt to obtain a 3:4-anhydro-compound was made. With CPh₃Cl in C₅H₅N at 100°, (VI) gives its 6-CPh₃ derivative (VIII) [4-acetate (IX), m.p. 165°, $[\alpha]_D^{15} +72.4^\circ$ in CHCl₃], in the form of a glass containing (VI). Alkaline hydrolysis of (IX) does not give a 3:4-anhydro-ring: mild agents give (VIII), while more powerful cause resinification. Apparently a Walden inversion from *trans*- to *cis*-formation is necessary before the 3:4-ring can be obtained.

E. W. W.

Ring-structure of *D*-altrosan. N. K. RICH-



(I.)

MYER and C. S. HUDSON (J. Amer. Chem. Soc., 1940, 62, 961—964).—*D*-Altrosan consumes 2 HIO₄, giving HCO₂H (1 mol.) and an aldehyde, oxidised to *L*'-oxy-*D*-methylenediglycollic acid, and thus is (I).

R. S. C.

Manufacture of fructose. I. Decomposition of fructose with acid. I. Determination of reaction constant at high temperature. K. FUJINO and Y. ARAO (Rept. Inst. Sci. Res. Manchoukuo, 1940, 4, 17—24).—At 120° and in presence of acid, decomp. of fructose (I) increases with increase in time of heating, concn. of (I), and vol. of acid used. The rate of change, which is > that of glucose, is greatest at the beginning of the reaction.

I. A. P.

Structure of difructose anhydride III (difructofuranose 1:2':2:3'-anhydride). E. J. McDONALD and R. F. JACKSON (J. Res. Nat. Bur. Stand., 1940, 24, 181—204; cf. Haworth *et al.*, A., 1932, 724).—Difructose anhydride I (difructofuranose 1:2':2:1'-anhydride) or III (the 1:2':2:3'-anhydride) (A) and Me_2SO_4 -aq. NaOH at 70°, then $\text{MeI}-\text{Ag}_2\text{O}$, afford 3:4:6:3':4':6'-hexamethyldifructofuranose 1:2':2:1'-anhydride, b.p. 170—175°/0.01 mm., $[\alpha]_D^{25} +23.7^\circ$ in CHCl_3 , and 3:4:6:1':4':6'-hexamethyldifructofuranose 1:2':2:3'-anhydride, b.p. 161—165°/0.417 mm., $[\alpha]_D^{25} +157.9^\circ$ in CHCl_3 , respectively. The latter compound is hydrolysed by 0.8N-HCl at 95° to 3:4:6- (I) and 1:4:6-trimethylfructofuranose; oxidation (HNO_3) gives monobasic acids and thence esters, which are oxidised by acid BaMn_2O_8 to trimethylarabonolactone, derived from (I). (A) and $\text{C}_6\text{H}_5\text{Cl}-\text{C}_6\text{H}_5\text{N}$ at 80°, then at room temp., give 6:1':6'-tri(triphenylmethyl)difructofuranose 1:2':2:3'-anhydride, m.p. 127°, $[\alpha]_D +64.2^\circ$ in CHCl_3 , converted by $\text{Ac}_2\text{O}-\text{C}_6\text{H}_5\text{N}$ at 100° (bath) into its triacetate, $[\alpha]_D +65.2^\circ$ in CHCl_3 , which is methylated by Me_2SO_4 -aq. NaOH-COMe₂ to 6:1':6'-tri(triphenylmethyl)-3:4:4'-trimethyldifructofuranose 1:2':2:3'-anhydride, $[\alpha]_D^{24} +70.2^\circ$ in CHCl_3 . C_6H_5 is removed from the latter by $\text{HBr}-\text{CHCl}_3$ at 0° and the anhydride formed is hydrolysed by 0.8N-HBr at 94° to partly methylated fructoses; these afford fructosides which are hydrolysed by 0.1N-HCl at 60° to 3:4-dimethyl- and 4-methyl-fructose, $[\alpha]_D^{25} -87.5^\circ$ at equilibrium (glucosazone, m.p. 156°). Methyl-3:4-dimethylfructoside and HNO_3 (d 1.42) at 65—95° give the dibasic 3:4-dimethyl-lactol acid, also derived from 1:3:4-trimethylfructose (cf. Hibbert *et al.*, A., 1931, 827). The C_6H_5 groups (see above) are substituents of the three primary OH. (A) is composed of two furanoid fructose residues, with two O bridges connecting C_{11} and C_{12} of one fructose residue with C_{12} and C_{13} of the other. Its great stability is due to the presence of a dioxan ring serving as connecting link between the two fructose groups. 6:6'-Ditriphenylmethyldifructofuranose 1:2':2:1'-anhydride, m.p. 195°, $[\alpha]_D^{25} +20.35^\circ$ in CHCl_3 , and Ac_2O at 110° yield the 3:4:3':4'-tetra-acetate (II), m.p. 194°, $[\alpha]_D^{25} +21.06^\circ$ in CHCl_3 , converted by Me_2SO_4 -COMe₂-aq. NaOH into the $(\text{C}_6\text{H}_5)_2\text{Me}_4$ derivative, and thence by 0.8N-HBr at 95° into a substance which with HCl-MeOH affords fructosides, hydrolysed by 0.1N-HCl at 60° to 3:4-dimethylfructose, $[\alpha]_D^{25} -60.66^\circ$ in H_2O . The latter is also obtained from triphenylmethyldimethylinulin, but is contaminated with 4-methylfructose. (II) and $\text{HBr}-\text{AcOH}$ at 0—5° give difructofuranose 1:2':2:1'-anhydride 3:4:3':4'-tetra-acetate, m.p. 173°, $[\alpha]_D^{25} -9.9^\circ$ in

CHCl_3 , methylated by Purdie's reagents to the 6:6'- Me_2 derivative, m.p. 127—128°, $[\alpha]_D +10.8^\circ$ in CHCl_3 , which is hydrolysed by 0.8N-HCl at 95° and the residue converted into fructosides which give 6-methylfructose (osazone, m.p. 183—184°). A mechanism is suggested by which the difructose anhydrides are formed during hydrolysis of inulin. Hexamethyldifructose anhydride II has m.p. 73°, b.p. 169—170°/0.43 mm., $[\alpha]_D^{25} -28.2^\circ$ in CHCl_3 . Constitutions of the disaccharides prepared by Schlubach *et al.* (A., 1933, 938) are ill-defined.

A. T. P.

Fission of methylglucosides of synthetic sugars by sweet almond emulsin.—See A., 1940, III, 535.

Synthesis of glycol glucosides. S. KARJALA and K. P. LINK (J. Amer. Chem. Soc., 1940, 62, 917—920).— $(\text{CH}_2\text{OH})_2$, acetobromoglucose (modified prep.; 86% yield), and Ag_2CO_3 , later in C_6H_6 , give ethylene glycol β -D-glucoside tetra-acetate, m.p. 105—106° [lit. 101—103° (corr.)], $[\alpha]_D^{25} -26.3^\circ$ in H_2O , hydrolysed to the free glucoside, dimorphic, m.p. 117.5—118° and 136—137°, respectively, $[\alpha]_D^{25} -28.5^\circ$ in H_2O , and converted by further similar reactions into ethylene glycol bis- β -D-glucoside octa-acetate, m.p. 169—170° (corr.) (lit. 170—171°), $[\alpha]_D^{25} -31.76^\circ$ in CHCl_3 . Similar reactions give diethylene glycol β -D-glucoside, m.p. 116.5—118°, $[\alpha]_D^{25} -22.4^\circ$ in H_2O [tetra-acetate, m.p. 92—93° (corr.)], $[\alpha]_D^{24} -27.62^\circ$ in H_2O , and bis- β -D-glucoside octa-acetate, m.p. 125.5—126.5°, $[\alpha]_D^{25} -23.5^\circ$ in CHCl_3 (gives an oil when hydrolysed), propylene glycol β -D-glucoside, m.p. 136—138°, $[\alpha]_D^{25} -25.5^\circ$ in H_2O (tetra-acetate, m.p. 99—101°, $[\alpha]_D^{25} -6.8^\circ$ in CHCl_3), triethylene glycol β -D-glucoside tetra-acetate, an oil, methoxyethyl β -D-glucoside, m.p. 139—140°, $[\alpha]_D^{25} -26.0^\circ$ in H_2O (tetra-acetate, m.p. 65—67°, $[\alpha]_D^{25} -19.5^\circ$ in CHCl_3), trimethylene glycol β -D-glucoside tetra-acetate, m.p. 97—98°, $[\alpha]_D^{25} -17.3^\circ$ in CHCl_3 , and bis- β -D-glucoside octa-acetate, m.p. 171—172°, $[\alpha]_D^{25} -15.8^\circ$ in CHCl_3 .

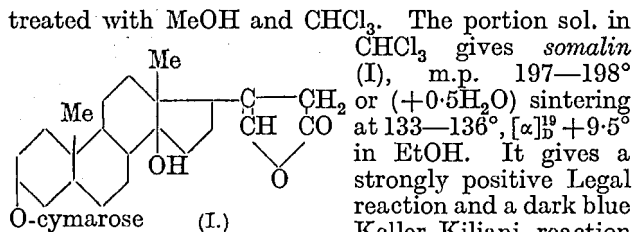
R. S. C.

Scilliroside. A. STOLL and J. RENZ (Compt. rend., 1940, 210, 508—509).—Alcoholic extracts (details given) of the dry powdered bulbs of red squill contain scilliroside, $\text{C}_{32}\text{H}_{46}\text{O}_{12} \cdot 0.5\text{H}_2\text{O}$, m.p. 168—170° (corr.; decomp.), $[\alpha]_D^{25} -59^\circ$ in MeOH [tetra-acetate, m.p. 199° (corr.)], $[\alpha]_D^{25} -49^\circ$ in MeOH, which gives the Liebermann test, but neither the Legal nor Baljet test, and contains 1 Ac and a lactone ring. Hydrolysis (acid) liberates glucose but no cryst. aglucone. Spectrographic measurements indicate that its skeleton is a perhydrocyclopentanophenanthrene together with a 6-atom lactone ring containing 2 double linkings (cf. Wieland *et al.*, A., 1936, 1252). Scilliroside acts like scillaren-A on the frog heart and is a powerful convulsant drug for rodents.

J. L. D.

Oleocyanin, $\text{C}_{27}\text{H}_{31}\text{O}_{15}\text{Cl}$.—See A., 1940, III, 462.

African arrow poison plants. I. *Adenium somalense*, Balf. fl. M. HARTMANN and E. SCHLITTLER (Helv. Chim. Acta, 1940, 23, 548—558).—The dried roots are percolated with 70% MeOH and, after treatment with basic Pb acetate, the percolate is



in AcOH. It is hydrolysed to digitoxigenin (characterised by its acetate and by conversion into Me isodigitoxigenate) and cymarose. Pharmacologically (I) is more closely related to strophanthin than to digitoxin.

H. W.

Viscosities of arabogalactan solutions. H. S. OWENS (J. Amer. Chem. Soc., 1940, **62**, 930—932).—Prep. of arabogalactan (87.7% anhydrogalactose) from Western larch heartwood is described. η of 6–10% aq. solutions at 20°, 40°, and 60° is best expressed by Kunitz's equation (A., 1936, 1005) and indicates a spherical mol. in solution and a mol. wt. ≈ 2208 , i.e., $[\text{C}_5\text{H}_8\text{O}_4 \cdot (\text{C}_6\text{H}_{10}\text{O}_5)_6]_2$. R. S. C.

Constitution of banana starch. E. G. E. HAWKINS, J. K. N. JONES, and G. T. YOUNG (J.C.S., 1940, 390—394).—Banana starch (I) resembles potato starch (II) in physical properties. It is hydrolysed normally by acid, giving only glucose. It is more resistant than (II) both to acetylation (either with Cl_2 and SO_2 catalysts, or using $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$) and to methylation. The methylated product (III), whether prepared directly or via the acetate, has mol. wt. $\sim 200,000$ (based on η ; cf. Hirst *et al.*, A., 1939, II, 359, 495), and on fractionation and hydrolysis gives 2 : 3 : 4 : 6-tetramethyl- (IV), 2 : 3 : 6-trimethyl-, and dimethyl-glucose only. The proportion of (IV) corresponds with a repeating unit of ~ 24 (22–26) glucose residues. Heated with 1% $\text{H}_2\text{C}_2\text{O}_4$ in $\text{MeOH}-\text{H}_2\text{O}$, (III) resembles rice starch (V) (*loc. cit.*, 495) in disaggregating smoothly to products of lower mol. wt. but unchanged chain length. The mol. structure in (I) and in (V) is thus essentially identical, both having glycosidic linkings. Methylated inulin, with 1 : 6-fructofuranoside linkings, is hydrolysed ~ 7 times as rapidly as (III).

E. W. W.

Recrystallisation of cellulose and its derivatives. G. GENTOLA (Atti X Congr. Internaz. Chim., 1938, IV, 117—123).—The crystallinity of regenerated cellulose (I) depends on the concn. of the solution, the nature of the solvent and precipitant, the temp. and rate of coagulation, and the mechanical stresses involved. The general theory, which is exemplified by observations on regeneration of cellulose nitrate (N 13.2%), assumes that (I) and its derivatives in solution do not retain a strictly rectilinear configuration.

F. O. H.

Mechanism of degradation of cellulose. S. M. KAJI and K. VENKATARAMAN (Current Sci., 1940, 9, 66—67).—A series of oxycelluloses (I) and hydrocelluloses (II) have been prepared by treating cellulose (III) with acids, oxidising agents, and ultra-violet light, and also by submitting (III) to singeing processes, heat-treatments, and mildew attack. Whilst four types of (I) have been distinguished, (II) seems to be of a single chemical type; correlations with the

Haworth formula for (III) are suggested. Three possible series of reactions, after the fission of the 1 : 4-glucosidic linkings, are outlined in the degradation of (III) with the formation from (I) of (a) a dialdehyde, (b) a dicarboxylic acid, (c) a β -ketonic aldehyde or acid.

W. R. A.

Trimethylamine oxide in different varieties of flesh and fish. IV. Mode of formation of formaldehyde from trimethylamine oxide. Y. HATTORI (J. Pharm. Soc. Japan, 1940, **60**, 30—33).— NMe_3O is heated at 180° in a rapid current of moist air and the product is treated with dil. HCl. The solution when cautiously evaporated at a low temp. leaves very hygroscopic, colourless needles converted into dimethyl- and methoxydimethyl-ammonium platinichloride, m.p. 168°. The substance is stable in strongly acid (HCl) solution but not in dil. acid; the free base passes when gently heated into NHMe_2 and CH_2O . In absence of H_2O elimination of CH_2O from NMe_3O does not take place. Keeping of $\text{NMe}_3 \cdot 2\text{H}_2\text{O}$ over conc. H_2SO_4 at 10–12 mm. until const. in wt. leads to hydroxytrimethylammonium hydroxide (I), $\text{NMe}_3(\text{OH})_2$, m.p. 201°, in which one OH is basic and the other is non-basic. (I) yields an acetate, $\text{OH} \cdot \text{NMe}_3 \cdot \text{OAc}$, m.p. 49° (non-cryst. Ac derivative), picrate, m.p. 202°, benzoate, m.p. 72° (non-cryst. Bz derivative), benzoyloxytrimethylammonium picrate, m.p. 270°, hydroxytrimethylammonium phenylurethane, m.p. 273°, acetoxytrimethylammonium phenylurethane, m.p. 274°, and trimethylammonium picrate phenylurethane, m.p. 221.5°. The conversion of NMe_3O into CH_2O occurs through (I), which passes when heated into H_2O and $\text{NMe}_2 \cdot \text{OMe}$ (volatile). This is stable towards heat when dry but reacts with H_2O at a low temp. giving $\text{OH} \cdot \text{NHMe}_2 \cdot \text{OMe}$, which breaks down into NHMe_2 , H_2O , and CH_2O .

H. W.

Derivatives of diethylenetriamine [di-(β -aminoethyl)amine]. P. JOB and J. BRIGANDO (Compt. rend., 1940, **210**, 438—440; cf. A., 1927, 546).—Pentaminocobaltic chloride when warmed with $\text{NH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_2$ (= etn) gives $(\text{Co etn}_2)\text{Cl}_3$ from which all Cl is pptd. by AgNO_3 (cf. A., 1938, I, 403). Equimol. amounts of etn and CuSO_4 in H_2O give Cu_3etn_4 ; when the constituents react in varying proportions the equilibrium const. (k) is $\sim 1.5 \times 10^{-13}$ at room temp. A similar complex Ag salt is $[\text{Ag etn}_2]^+$, k being 1.07×10^{-8} at 22°. etn acts as a trivalent radical in the Co and Cu salts and is univalent in the Ag salt.

J. L. D.

Amino-sugars. II. Action of dilute alkali on N-acylglucosamines. T. WHITE (J.C.S., 1940, 428—437).—The view that N-acylglucosamines, after treatment with hot dil. alkali, give a red-purple coloration with Ehrlich's reagent, through formation of heterocyclic derivatives (by loss of H_2O), is confirmed. N-Acetylglucosamine (I) [improved prep. from glucosamine hydrochloride (II) and $\text{Ac}_2\text{O}-\text{AgOAc}-\text{MeOH}$] is stable to dil. alkali at room temp., but at the b.p. the change into a chromophoric product, now regarded as 2-methyl-4 : 5 : 2' : 1'-glucopyrano- Δ^2 -oxazoline (III), m.p. 70–75°, may be followed colorimetrically (cf. Morgan *et al.*, A., 1934, 910). (III) (prep. under various conditions de-

scribed) is hygroscopic and amorphous, and gives the Ehrlich test. It has $[\alpha]_D^{25} +30^\circ$ in MeOH or H_2O (shows no mutarotation), is oxidised by Br in H_2O to glucosamine hydrobromide, and is hydrolysed by boiling 0.02N-MeOH-HCl to (I). With Me_2SO_4 -NaOH, (III) gives *N*-acetylmethyl-3:4:6-trimethylglucosaminide (IV) (cf. Cutler *et al.*, A., 1938, II, 46); with MeI-Ag₂O-MeOH it is incompletely methylated. $Ac_2O-C_5H_5N$ converts (III) into its 3':4':6'-triacetate, a hygroscopic glass, $[\alpha]_D^{25} +36.7^\circ$ in $CHCl_3$. This is also obtained, m.p. 70° , $[\alpha]_D^{25} +54^\circ$ in $CHCl_3$, from 1-bromo-*N*-acetylglucosamine 3:4:6-triacetate (Moggridge *et al.*, A., 1938, II, 266) with aq. NaOAc at 65° (mechanism of ring-formation suggested). With $Me_2SO_4-CCl_4$ in 60% NaOH at $75-100^\circ$, (I) gives (IV), steam-hydrolysed by 4N-HCl to 3:4:6-trimethylglucosamine hydrochloride, which with $Ac_2O-AgOAc-MeOH$ gives *N*-acetyl-3:4:6-trimethylglucosamine, m.p. 234° , $[\alpha]_D^{25} +75^\circ \rightarrow +44.8^\circ$ in H_2O . This with 0.02N-Ba(OH)₂ at 100° (bath) gives 2-methyl-4:5:2':1'-(3':4':6'-trimethylglucopyrano)- Δ^2 -oxazoline, a syrup, giving the Ehrlich test. *N*-Ac-Bromo- (V) with 0.1N-NaOH at 100° (15 min.) gives *N*- α -hydroxy-propionylglucosamine (VI), m.p. 217° , $[\alpha]_D^{25} +69.1^\circ \rightarrow 66.2^\circ$ in H_2O . With 0.05N-NaOH or -Ba(OH)₂ at 100° , (V) gives 3-keto-2-methyl-5:6:2':1'-glucopyrano-3:4:5:6-tetrahydro-1:4-oxazine (VII), m.p. $140-145^\circ$, $[\alpha]_D^{25} +19.4^\circ$ in H_2O , giving the Ehrlich test. In 13% aq. NaOH, (VII) gives (VI). With boiling 1% MeOH-HCl, (VII) yields (II). Methylation of (VII) by MeI-Ag₂O gives a syrup. With $Ac_2O-C_5H_5N$, (VII) forms its 3':4':6'-triacetate, amorphous, $[\alpha]_D^{25} +32.1^\circ$ in $CHCl_3$.

E. W. W.

Oxidation of aldoses by hypoiodite. VII. Glucosamine and *N*-acetylglucosamine. K. MYRBÄCK (Svensk Kem. Tidskr., 1940, 52, 21-30; cf. A., 1940, II, 67).—Glucosamine (I) and its hydrochloride (II) can be determined as accurately as glucose by Bertrand's method. The change does not occur stoichiometrically but the calculation of Cu to (I) is effected with the help of an empirical graph. In presence of NaOH (I) consumes much more I from OI' than corresponds with the production of glucosamic acid (III), the amount increasing with [NaOH]. In presence of Na_2CO_3 or $NaHCO_3$ utilisation of 4 I occurs rapidly but the subsequent action is very slow. Br- H_2O oxidises (I) or (II) normally to (III), thus suggesting a betaine structure for (I). This view is confirmed by the observation that *N*-acetylglucosamine (IV), m.p. 204° , $[\alpha]_D^{25} +70.5^\circ$ to $+41.3^\circ$ in H_2O (which is so slowly hydrolysed by alkali that betaine formation is excluded under the experimental conditions), behaves towards OI' as a normal aldose. Exchange of OH at C₂ for NHAc has only a small influence on the rate of oxidation whereas the epimeric mannose is much more slowly oxidised. The behaviour of (IV) towards Fehling's solution depends greatly on experimental conditions. H. W.

Compound, $C_{21}H_{44}O_{12}N_6SSe_2$, decomp. $263-265^\circ$, from grain.—See A., 1940, III, 461.

Complex compounds of diguanide with bivalent metals. I. Copper diguanidines. P. RÂY and P. N. BAGCHI (J. Indian Chem. Soc., 1939,

16, 617-620).— Cu^{II} bisdiguanide dihydrate when heated to 110° for 14 hr. gives Cu^{II} bisdiguanidine. Co-ordination with diguanide confers stability on many unstable simple Cu salts. Cu^{II} bisdiguanidinium chloride (+2H₂O), bromide (+2H₂O), iodide (+3H₂O), fluoride (+4H₂O), nitrite (+H₂O), carbonate (+4H₂O), sulphite (+4H₂O), thiosulphate (+3H₂O), thiocyanate, dithionate (+2H₂O), chromate (+3H₂O), and hypophosphite (+2H₂O) are described. F. R. S.

Production of amidines and their derivatives.—See B., 1940, 344.

Complex compounds of diguanide with trivalent metals. VI. Cobaltic trisdiguanidines. P. RÂY and N. K. DUTT. VII. Cobaltic trisphenyldiguanidines. P. RÂY and H. P. BHATTACHARYA (J. Indian Chem. Soc., 1939, 16, 621-628, 629-633).—VI. Co combines with diguanide to form complex compounds similar to the corresponding Cr compounds (cf. A., 1938, II, 435): *Co*^{III} trisdiguanide dihydrate, cobaltic trisdiguanidine, cobaltic trisdiguanidinium chloride, fluoride, bromide, iodide, thiocyanate, chlorate, perchlorate, borofluoride, nitrate, nitrite, chloroformate, carbonate, sulphate (+7H₂O), selenate (+7H₂O), chloroselenate, hydroxo-sulphite, sulphite (+7H₂O), chlorothiosulphate (+2.5H₂O), thiosulphate, chlorochromate, chromate (+3H₂O), perchromate (+4H₂O), chlorophosphate, phosphate (+6H₂O), hydro-sulphide and -polysulphide, iodate, chloroiodate (+H₂O), periodate (+3H₂O), oxalate, and camphorsulphonate.

VII. *Co*^{III} trisphenyldiguanide forms a trihydrate, m.p. $\sim 200^\circ$ (decomp.), and dihydrate melts with decomp.; both are dehydrated to *Co*^{III} trisphenyldiguanidine, similar to the corresponding Cr compound. *Co*^{III} trisphenyldiguanidinium chloride (+2.5H₂O), bromide (+H₂O), iodide (+H₂O), sulphate (+10H₂O), nitrate (+0.5H₂O), nitrite (+0.5H₂O), carbonate (+2H₂O), thiosulphate (+7H₂O), thiocyanate (+3H₂O), dithionate (+2H₂O), and chromate (+2H₂O) are also described. F. R. S.

Aliphatic arsinic acids. Arsenation of mono-, di-, and tri-chloroacetic and mono- and di-bromomalonic acids. A. R. MARQUEZ (Rev. Fac. Cienc. Quím. La Plata, 1939, 14, 217-228).—The yield of arsinioacetic acid (I) from $CH_2Cl \cdot CO_2H$ (1 mol.) and Na_3AsO_3 (x mols.) increases with x and reaches 100% when $x = 2$. The effect of varying the [NaOH] and time of reaction has been studied. The solubility of (I) in H_2O is recorded between 0° (0%) and 40° (98.5%). Reduction of (I) with NaH_2PO_2 in aq. H_2SO_4 yields arsenoacetic acid (NH_4 salt). The As in these acids is determined by the I liberated from KI in HCl. F. R. G.

X-Ray studies of mercury alkylthiol chlorides. A. JOHANSSON (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 14, 11 pp.).— $SR \cdot CH_2 \cdot CO_2H$ are converted by 0.01M- H_2O_2 into $RSO \cdot CH_2 \cdot CO_2H$, and thence by aq. $HgCl_2$ at 100° into $HgCl \cdot SR$, $CHO \cdot CO_2H$, and HCl. Thus are obtained *Hg Me*, m.p. $>230^\circ$, *Et*, m.p. $>230^\circ$, *Pr*^a, m.p. $182-183^\circ$, *Pr*^b, m.p. $>230^\circ$, *Bu*^a, m.p. $175-176^\circ$, *Bu*^b, sinters at $215-220^\circ$, and *CHMeEt chloride*, m.p. $188-189^\circ$. *HgBuCl*, decomp. when heated, is obtained by working at room temp. throughout, since at 100° it decomposes mainly to

$\text{CH}_2\cdot\text{CMe}_2$, HgS , and HCl . X-Ray consts. etc. are recorded for the products and may be used for identification.

R. S. C.

Mechanism of Walden inversion in reactions leading to formation of the carbonato-diethylenediaminecobaltic ion.—See A., 1940, I, 266.

Co-ordination stability of ethylene hydrocarbons. (Miss) A. GELMAN (Ann. Sect. Platine, 1939, No. 16, 35—39).—The stability of complexes of the type $\text{NH}_4[\text{PtCl}_3\text{R}]$ falls in the order $\text{R} = \text{CO} > \text{CH}_2\cdot\text{CHPh} > \text{C}_2\text{H}_4 > \text{CH}_2\cdot\text{CHMe} = \text{CH}_2\cdot\text{CHEt}$.

R. T.

Compounds of platinum salts with ethylenic hydrocarbons.—See A., 1940, I, 267.

Compounds of platinum and iridium salts with acetonitrile.—See A., 1940, I, 267.

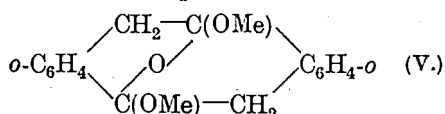
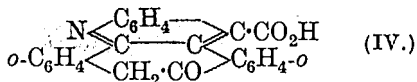
Ethylene compounds of platinum nitrochlorides.—See A., 1940, I, 267.

Low-temperature dehydrogenations. II. R. T. ARNOLD, C. COLLINS, and W. ZENK (J. Amer. Chem. Soc., 1940, 62, 983—984).—Chloranil in boiling xylene converts 1-*p*-diphenyl-, 1-*p*-diphenyl-2-methyl-, 1- α - and 1- β -naphthyl-, and 1-*o*-tolyl- Δ^1 -cyclohexene into the derived aromatic compounds in 47, 72, 67, 72, and 72% yield, respectively (cf. A., 1939, II, 362).

R. S. C.

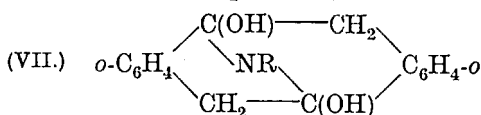
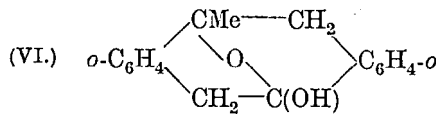
Attempt to synthesise a substituted cyclooctatetraene. S. WAWZONEK (J. Amer. Chem. Soc., 1940, 62, 745—749).—3 : 4 : 7 : 8-Dibenz- $\Delta^{3:7}$ -cyclooctadiene-1 : 5-dione (I) reacts as an aliphatic α -diketone. $(\text{CHPh}\cdot\text{CO}_2\text{H})_2$ is prepared from the dinitrile by boiling $\text{H}_2\text{SO}_4\text{--H}_2\text{O--AcOH}$ (2 : 2 : 1). Diphen succindane-9 : 12-dione with PCl_5 and later AcOH gives 9 : 12-dichloro- $\Delta^{9:11}$ -diphen succindadiene (II) (cf. A., 1922, i, 444) and 9 : 9 : 12 : 12-tetrachloro- Δ^{10} -diphen succindene (III), $\text{o-C}_6\text{H}_4\langle\text{CCl}_2\text{C}\rangle\text{C}_6\text{H}_4\text{-o}$, m.p. 178—179°, converted by Zn dust in boiling AcOH into (II). With 12% O_3 in EtOH at -40° , (III) gives the ozonide, m.p. 191—193° (decomp.), converted by $\text{H}_2\text{--5\% Pd--BaSO}_4$ at 2.3 atm. in EtOAc into (I), m.p. 203.5—204.5° [dioxime, m.p. 240—243° (decomp.); $(\text{CHPh})_2$ derivative, m.p. 244—246°], difficultly sol. in aq., but readily sol. in alcoholic, alkali to give a yellow solution becoming (reversibly) orange when heated. No colour is formed by (I) in $\text{PhN}_2\text{Cl--EtOH--alkali}$. With hot PCl_5 , (I) gives the dichlorodiphosphinic acid,

$\text{o-C}_6\text{H}_4\langle\text{CCl}(\text{PO}_3\text{H}_2)\cdot\text{CH}_2\rangle\text{C}_6\text{H}_4\text{-o}$, and with isatin and 20% KOH gives the substance (IV), m.p. 297° (gas). With Me_2SO_4 and 20% KOH in MeOH , (I) gives the Me_2 ether (V), m.p. 143—144°, unchanged by Br, but

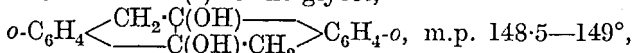


hydrolysed to (I) by HBr--AcOH . In the Grignard machine, (I) shows only 1 CO and 1 active H. With

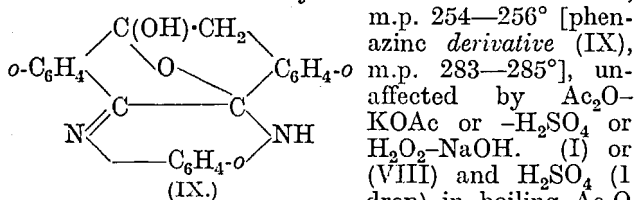
MgMeI in boiling $\text{Et}_2\text{O--C}_6\text{H}_6$, (I) gives the compound (VI), m.p. 213—215°, and with boiling $\text{NH}_3\text{--H}_2\text{O--EtOH}$ gives the substance (VII; $\text{R} = \text{H}$), m.p. 167° (gas), converted by HNO_3 or above the m.p. into (I).



With $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl--Na}_2\text{CO}_3\text{--EtOH--H}_2\text{O}$, (I) gives the substance (VII; $\text{R} = \text{NH}\cdot\text{CO}\cdot\text{NH}_2$), m.p. 210° (decomp.), converted by heat alone or with KOH into Δ^{10} -diphen succindene and diphen succindane. $\text{Zn--Hg--HCl--AcOH--H}_2\text{O}$ or 20% KOH--Zn dust- EtOH reduces (I) to the glycol,



which with H_2SO_4 or HI--AcOH gives a yellow substance, m.p. $>350^\circ$, and with Pb(OAc)_4 in C_6H_6 at 50° re-forms (I). Boiling $\text{Ac}_2\text{O--KOAc}$ converts (I) into the acetate (VIII), m.p. 138—139°, of the monoenol, hydrolysed by alkali to (I) and oxidised by $\text{CrO}_3\text{--AcOH}$ at $50\text{--}60^\circ$ to $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H-o}$. With Br--AcOH , (VIII) gives a *Br-acetate*, m.p. 219—223° (gas), unchanged by KOAc--AcOH but converted by Br--CHCl_3 into a crude Br_2 -derivative diacetate, m.p. 173—178° (gas), which with $\text{NH}_3\text{--EtOH--H}_2\text{O}$ gives 3 : 4 : 7 : 8-dibenz- $\Delta^{3:7}$ -cyclooctadiene-1 : 2 : 5-trione,



give the diacetate, m.p. 150—151°, which yields a *Br*-derivative diacetate, m.p. 225—229°, obtained also from (VIII) by $\text{H}_2\text{SO}_4\text{--AcOH}$ and unaffected by KOAc--AcOH or Br .

R. S. C.

Oxidation of cyclic compounds by hydrogen peroxide catalysed by pervanadic acid. W. TREIBS (Angew. Chem., 1939, 52, 698—700).—A review.

R. S. C.

Condensation of esters with aromatic hydrocarbons by means of aluminium chloride. J. F. NORRIS and P. ARTHUR, jun. (J. Amer. Chem. Soc., 1940, 62, 874—877; cf. A., 1939, II, 372).— MeOAc and AlCl_3 give a 1 : 1 additive compound, m.p. 60°, which at 143° (rapidly at 170°) gives MeCl (0.7 mol.), at $184\text{--}200^\circ$ gives HCl (0.38 mol.) and a residue, ? $\text{AlCl}_2\cdot\text{OAc}$ (I). EtOAc gives a similar compound, which gives EtCl (0.67 mol.) and (I). With C_6H_6 (2 mols.) and AlCl_3 (1.2 mols.), (I) (1 mol.) gives 42% of COPhMe . The liquid compound from Bu^nOAc gives 5% of Bu^nCl and 1.26 mols. of HCl with much C_4H_8 . $\text{HCO}_2\text{Me}\cdot\text{AlCl}_3$, decomp. 110° , gives MeCl (88%) at 143° , followed by CO and HCl at 185° ; the residue gives no PhCHO . HCO_2Et behaves similarly.

EtOAc, C_6H_6 , and $AlCl_3$ (2 mols. required in this and similar reactions) at room temp. give PhEt (12.3%) and $m\text{-}C_6H_4Et_2$ (51.3%); longer treatment gives also a little $s\text{-}C_6H_3Et_3$. HCO_2Et gives the same products, but the yield of $s\text{-}C_6H_3Et_3$ can be raised to 50.5%. HCO_2Me at 60–80° gives PhMe, m -xylene, and $s\text{-}C_6H_3Me_3$, the yields varying according to the ratio $C_6H_6 : HCO_2Me$, but being very low at room temp. At 100° PhMe, MeOAc, and $AlCl_3$ give mainly 2 : 4 : 1- $C_6H_3Me_2\text{-}COMe$ with some $p\text{-}C_6H_4Me\text{-}COMe$, m -xylene, and $s\text{-}C_6H_3Me_3$. MeOAc or EtOAc and C_6H_6 at 60–80° give similar results. 2 : 4-, m.p. 174.2–175.2°, 2 : 5-, m.p. 174.2–175.2° (corr.), and 3 : 4-dimethylacetophenone-2 : 4-dinitrophenylhydrazones, m.p. 255.2–255.8° (corr.), 2 : 4-, m.p. 154.6–154.8°, and 2 : 5-dimethylacetophenone- p -nitrophenylhydrazones, m.p. 159.8–160.1° (corr.), are described.

R. S. C.

Sulphonation and nitration reactions promoted by boron trifluoride.—See B., 1940, 342.

Production of pure hydrocarbons of the benzene series by distillation.—See B., 1940, 343.

Chain polymerisation of styrene.—See A., 1940, I, 259.

Constituents of some Indian essential oils. XXVII. Synthesis of $dl\text{-}\alpha$ -curcumene. F. D. CARTER, J. L. SIMONSEN, and H. O. WILLIAMS (J.C.S., 1940, 451–453).—The *Et* ester, b.p. 157°/19 mm., of $dl\text{-}\gamma\text{-}p\text{-tolyl-}n\text{-valeric acid}$ (improved prep.) and Na-EtOH give $\delta\text{-}p\text{-tolyl-}n\text{-amyl alcohol}$, b.p. 151°/16 mm. (3 : 5-dinitrobenzoate, m.p. 80–81°), which is converted (NaCN-I) through the chloride, b.p. 141°/17 mm., into $\delta\text{-}p\text{-tolyl-}n\text{-hexoic acid}$ (I), b.p. 197°/20 mm. [*Me* (II), b.p. 167°/17 mm., and *p*-phenacyl esters, m.p. 70°]. Condensation ($AlCl_3$) of PhMe and glutaric anhydride affords a mixture of $\alpha\gamma\text{-di-}p\text{-toluoylpropane}$, m.p. 110° (bis-2 : 4-dinitrophenylhydrazones, m.p. 257°), and $\gamma\text{-}p\text{-toluoyl-}n\text{-butyric acid}$, m.p. 148–149° (semicarbazone, decomp. 218°), the *Me* ester, b.p. 192–194°/18 mm., of which with $MgMeI$ yields $\delta\text{-}p\text{-tolyl-}\Delta^7\text{-hexenoic acid}$, m.p. 80–81°. This acid is reduced ($Pd\text{-}H_2$) to (I), which could not be resolved owing to the instability of the alkaloidal salts. $MgMeI$ and (II) give $dl\text{-}\beta\text{-hydroxy-}\zeta\text{-}p\text{-tolyl-}\beta\text{-methylheptane}$, b.p. 164°/17 mm. (xenyliurethane, m.p. 84–85°), which with $KHSO_4$ is dehydrated to $dl\text{-}\alpha\text{-curcumene}$, b.p. 134°/16 mm. (nitrosate, decomp. 114°), identical with the natural hydrocarbon (cf. Simonsen *et al.*, A., 1939, II, 516).

F. R. S.

Magnesium pentamethylphenyl bromide. H. CLEMENT (Ann. Chim., 1940, [xi], 13, 243–316; cf. A., 1939, II, 60).—Methylation of xylene by $AlCl_3$ and $MeCl$ at 95° is a series of successive, not simultaneous, reactions so that it is possible to fix the most suitable durations (based on g. of HCl evolved) for the prep. of each derivative either in the best yield or for the readiest purification. C_6Me_5Br and Mg give $C_6Me_5\text{-}MgBr$ if an alkyl halide is also present and this reacts normally with CO_2 , CH_2O , $MeCHO$, and $COMe_2$. With $CH(OEt)_3$ it affords pentamethylbenzaldehyde, m.p. 130.5° (oxime), and with $PhCHO$ it yields pentamethylbenzhydrol, m.p. 107.5°. Abnormal reactions occur with EtOAc which gives penta-

methylacetophenone, m.p. 150–151°, and $BzCl$ which yields pentamethylbenzophenone, m.p. 125° (semicarbazone, m.p. 170°), which is also obtained from EtOBz. A principal abnormal and a secondary normal reaction are given with HCO_2Et and $AcCl$.

H. W.

New isomeride of trinitrotoluene. M. MILONE and A. MASSA (Gazzetta, 1940, 70, 196–201).—*m*-Nitrophenyldinitromethane (I), m.p. 124–125° (*K*, *Ag*, *Ba*, and *Pb* salts, deflagrating when heated; NH_4 salt), is obtained from $CHPh(NO_2)_2$ in HNO_3 (*d* 1.52) at room or higher temp. HNO_3 (*d* 1.4) has no action alone or in EtOH or AcOH; $H_2SO_4\text{-}HNO_3$ gives $p\text{-}NO_2\text{-}C_6H_4\text{-}CO_2H$. (I) is hydrolysed to $m\text{-}NO_2\text{-}C_6H_4\text{-}CO_2H$. In explosive properties (I) resembles 1 : 2 : 4-6- $C_6H_2Me(NO_2)_3$. The explosive power, and sensitiveness as detonators, of (I) and its salts are examined by the methods of Trauzl and of Berta. The compounds are inferior as detonators to those in common use.

E. W. W.

3 : 4'-Dinitrodiphenyl. W. A. WATERS (J.C.S., 1940, 474).—The product (I), m.p. 137°, obtained by Hodgson *et al.* (A., 1940, II, 126°) from diazotised $m\text{-}NO_2\text{-}C_6H_4\text{-}NH_2$ and $PhNO_2$, is not 3 : 4'-dinitrodiphenyl (cf. Scarborough *et al.*, A., 1927, 236), which has m.p. 189°. (I) is presumably a mixture.

E. W. W.

Halogenation of *as*-diphenylethane. F. E. SHEIBLEY and C. F. PRUTTON (J. Amer. Chem. Soc., 1940, 62, 840–841).— Cl_2 converts $CHPh_2Me$ in quartz in light at 100–150° into a yellow liquid, which, when distilled, gives $CHPh_2Me$, $(CHPh)_3$, and $\alpha\alpha\text{-dichloro-}\beta\beta\text{-diphenylethylene}$ (I), m.p. 79–80° (corr.). The mechanism is : $CHPh_2Me \rightarrow CPh_2MeCl$ (rate-determining step) $\rightarrow CPh_2\text{-}CH_2 \rightarrow CPh_2Cl\text{-}CH_2Cl \rightarrow CPh_2\text{-}CHCl \rightarrow CPh_2Cl\text{-}CHCl_2 \rightarrow$ (I). The $(CHPh)_2$ is formed from the $CPh_2\text{-}CHCl$. Bromination and distillation give only small amounts of $(CHPh)_2$ and $(CPh_2\text{-}CH)_2$. (I) is hydrolysed completely (to $CHPh_2\text{-}CO_2H$) only by $KOH\text{-}MeOH$ at 150°. With $PhOH$ at 225°, (I) gives benzilic aldehyde Ph_2 acetal, m.p. 111.5–112° (corr.). At 700° in SiO_2 , $CHPh_2Me$ gives C_6H_6 , PhMe, and $CHPh\text{-}CH_2$.

R. S. C.

Octadeca-(per-)chloroquaterphenyl. Preparation of deca-(per-)chlorodiphenyl. J. B. WIBAUT, J. OVERHOFF, and K. GRATAMA (Rec. trav. chim., 1940, 59, 298–302).—Commercial pentachlorodiphenyl and Cl_2 , first at 100° and then with $FeCl_3$ and I at 200–300°, give $(C_6Cl_5)_2$ (I) (75%), m.p. 309° (corr.). 4-4'-Diphenyldiphenyl [quaterphenyl] with $SbCl_5$, first at 220° and then at 270°, gives the Cl_{16} -derivative, m.p. 364–365° (corr.), sublimes at 340°/0.5 mm., the mol. wt. of which is determined by cryoscopy in (I) ($k = 36.0$).

R. S. C.

Stereochemistry. XXI. Diastereoisomeric phenyl β -carboxyethyl sulphoxides. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 15, 8 pp.).—The appropriate active $SPh\text{-}CH_2\text{-}CO_2H$ and H_2O_2 yield mixed isomerides, separated into *d*, *d*- and *l*, *l*-, m.p. 139–140° (decomp.), $[M]_D^{25} + 397.8^\circ$, -397.1° , *d*, *l*- and *l*, *d*-*Ph* β -carboxyethyl sulphoxide, $PhSO\text{-}CH_2\text{-}CO_2H$, m.p. 149–149.5° (decomp.), $[M]_D^{25} + 64.3^\circ$, -64.5° in abs. EtOH, the stereochemical prefixes referring to the C and S, respectively. Mix-

ture of the appropriate isomerides gives two inactive acids, m.p. 137–138°. Hot alkali racemises the C, but not the S. R. S. C.

α - and β -Phenylthioethanesulphonic acid and the corresponding sulphones. I. HEDLUND (Arkiv Kemi, Min., Geol., 1939, **13**, A, No. 12, 14 pp.).—PhSNa and $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ in H_2O give β -phenylthioethanesulphonic acid, $+2\text{H}_2\text{O}$, m.p. 48.5–49° (corr.) (Cu, $+4\text{H}_2\text{O}$, Zn, $+4\text{H}_2\text{O}$, Ca, and Cd salts), isolated as Na salt, $+ \text{H}_2\text{O}$. The Ba salt, $+2\text{H}_2\text{O}$, is converted by $\text{BaMnO}_4\cdot\text{CO}_2$ in H_2O into Ph β -sulphoethyl sulphone, $+2\text{H}_2\text{O}$ (Ba salt, $+ \text{H}_2\text{O}$), which is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ at 100° mainly to PhSO_2H and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{SO}_3\text{H}$, although some SO_2 is also evolved. β -(MeCSH) $_3$ (prep. modified to give 88% yield) and Cl_2 in H_2O give 35–45% of $\text{CHMeCl}\cdot\text{SO}_2\text{Cl}$, and thence $\text{CHMeCl}\cdot\text{SO}_3\text{Na}$, which with PhSNa in H_2O at 160° gives α -phenylthioethanesulphonic acid (I), m.p. ($+ \text{H}_2\text{O}$) 91.5–92°, ($+2\text{H}_2\text{O}$) 70–75° (Na, $+ \text{H}_2\text{O}$, Cu, and sol. Ba, $+ \text{H}_2\text{O}$, salts; loses SO_2 when kept over P_2O_5). Resolution of (II), best by brucine, gives the Ba, $+3\text{H}_2\text{O}$, $[\text{M}]_{\text{D}}^{25} +289.1^\circ$, and brucine salt, $[\text{M}]_{\text{D}}^{25} +266^\circ$ in H_2O , of the *d*-acid and the brucine salt, $[\text{M}]_{\text{D}}^{25} -288.8^\circ$ to -290° in H_2O , of the *l*-acid. BaMnO_4 yields dl-, m.p. 74–75°, *d*- (Ba salt, $[\text{M}]_{\text{D}}^{25} +34.7^\circ$), and *l*-Ph α -sulphoethyl sulphone (II) (Ba salt, $[\text{M}]_{\text{D}}^{25} -36.3^\circ$). (I) is racemised by NaOH and more slowly by HCl at 100°. (II) is very rapidly racemised by alkali, but is stable to acid. R. S. C.

Oxidation of tetrahydronaphthalene in condensed phase.—See A., 1940, I, 259.

Synthesis of 2-phenylnaphthalenes. D. H. HEY and S. E. LAWTON (J.C.S., 1940, 374–383).— $2\text{-C}_{10}\text{H}_7\text{Ph}$ (I) is readily obtained in quantity from $2\text{-C}_{10}\text{H}_7\text{N}\cdot\text{Ac}\cdot\text{NO}$ (II) and C_6H_6 (cf. Haworth *et al.*, A., 1940, II, 162). The optimum conditions for the prep. of (II) from $\text{C}_{10}\text{H}_7\cdot\text{NHAc}$ and nitrous fumes or NOCl in Ac_2O – AcOH are described. The yield of (I) is 25–30%, but the method is cheap. CrO_3 oxidises (I) to 2-phenyl-1:4-naphthaquinone (III). With HNO_3 (*d* 1.42) in AcOH , (I) gives 1-nitro- (IV), m.p. 127°, with some 1:5(?) dinitro-2-phenylnaphthalene, m.p. 187–188°; under more drastic conditions, inseparable mixtures are formed. The constitution of (IV) is established by synthesis from diazotised 1:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$. With hot $\text{SnCl}_2\text{-HCl-EtOH}$, (IV) gives 4-chloro-2-phenyl-1-naphthylamine, m.p. 79° (*Ac* derivative, m.p. 213°); with Fe in boiling AcOH , (IV) gives 2-phenyl-1-naphthylamine (V), m.p. 104° [*Ac* derivative (VI), m.p. 234°], converted by diazotisation in HCl and $\text{Cu}_2(\text{CN})_2$, into 1-chloro-2-phenylnaphthalene, m.p. 82°. Attempted nitrosation of 1:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ was unsuccessful. With HNO_3 (*d* 1.45) in AcOH at 40°, (VI) gives the *Ac* derivative (VII), m.p. 230°, of 4-nitro-2-phenyl-1-naphthylamine (VIII), m.p. 155°, obtained from (VII) by hydrolysis. With $\text{SnCl}_2\text{-HCl-EtOH}$, (VIII) gives 2-phenylnaphthylene-1:4-diamine, m.p. 100–101° (*Ac* $_2$ derivative, m.p. 320°), oxidised by boiling 5% aq. CrO_3 to (III). With PhNO_2 , (II) gives a mixture of 2-o- (IX), m.p. 101°, and 2-p-nitrophenylnaphthalene (X), m.p. 174°, separable only by vac.-sublimation or steam-distillation. With $\text{CrO}_3\text{-AcOH}$ on the steam-

bath, these yield respectively 2-o-, m.p. 164°, and 2-p-nitrophenyl-1:4-naphthaquinone, m.p. 223–224°. With excess of CrO_3 in boiling AcOH , (X) gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. $\text{SnCl}_2\text{-HCl}$ reduces (IX) to 2-aminophenylnaphthalene (*Ac* derivative, m.p. 204–205°) (identical with the product of Hofmann degradation of α -chlrysenamide), and (X) to 2-p-aminophenylnaphthalene, m.p. 99° (*Ac* derivative, m.p. 206°). With HNO_3 (*d* 1.5) in AcOH at 60–70°, (IX) gives 1-nitro-2-o-nitrophenylnaphthalene, m.p. 189°; at 60–70° with excess of HNO_3 , (X) gives a mixture containing $(\text{NO}_2)_3$ -derivatives (probably 1:5:4'- and 1:8:4'-) of (I). The *Ac* derivatives of 5:2-, 6:2-, and 8:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (prep. from phthaloyl-2-naphthylamine improved by hydrolysing the nitrated product with HCl continuously added to boiling EtOH) are converted by nitrous fumes in $\text{AcOH-Ac}_2\text{O}$ into 5-, m.p. 84° (decomp.), 6-, and 8-nitronitrosoaceto-2-naphthalide, both m.p. 86° (decomp.), and these by C_6H_6 into 5- (XI), m.p. 89°, 6- (XII), m.p. 146°, and 8-nitro-2-phenylnaphthalene (XIII), m.p. 69°. With Fe-HCl , (XI) gives 6-phenyl-1-naphthylamine, m.p. 142–143° (*Ac* derivative, m.p. 131°), and (XIII) gives 7-phenyl-1-naphthylamine, m.p. 94° (*Ac* derivative, m.p. 203°). With $\text{SnCl}_2\text{-HCl}$, (XII) gives 6-phenyl-2-naphthylamine (XIV), m.p. 132° (*Ac* derivative, m.p. 199°). 2:7- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$, acetylated and treated in $\text{AcOH-Ac}_2\text{O}$ with nitrous fumes, gives 2:7-dinitrosodiacylamidonaphthalene, m.p. 79° (decomp.), which with C_6H_6 yields 2:7-diphenylnaphthalene, m.p. 143°. The *Ac* $_2$ derivative, m.p. 334–335°, of 2:6- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ could not be nitrosated. With Br-AcOH , (I) gives 1-bromo-2-phenylnaphthalene, m.p. 66°, also obtained from (V) (Sandmeyer). 6:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NHAc}$ gives a *NO*-derivative, m.p. 82° (decomp.), which in C_6H_6 yields 6-bromo-2-phenylnaphthalene, m.p. 132°, also obtained from (XIV) (Sandmeyer). 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{OH}$ is nitrated by HNO_3 (*d* 1.42) in AcOH to 1:6:2- $(\text{NO}_2)_3\text{C}_{10}\text{H}_5\cdot\text{OH}$. 6:2- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ gives a *NO*-derivative, m.p. 82° (decomp.), which in C_6H_6 yields 6-methoxy-, m.p. 148°, hydrolysed by HI-AcOH to 6-hydroxy-2-phenylnaphthalene, m.p. 175–176°. 7:2- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ gives a *NO*-derivative, m.p. 85° (decomp.), yielding 7-methoxy-, m.p. 80°, and thence 7-hydroxy-2-phenylnaphthalene, m.p. 156°. With boiling Ac_2O , 7:2- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ gives diacetyl-7-methoxy-2-naphthylamine, m.p. 129°. E. W. W.

Reactions in sunlight. IV. E. OLIVERI-MANDALÀ and E. DELEO (Gazzetta, 1940, **70**, 186–190; cf. A., 1939, II, 316).—Acenaphthene in COMe_2 in sunlight (at Messina) for 22 months gives acenaphthenone. Fluorene in COMe_2 in sunlight for 8 months gives fluorenone. E. W. W.

9-Methyl-3:4-benzfluorene. L. F. FIESER and L. M. JOSHEL (J. Amer. Chem. Soc., 1940, **62**, 957–958).—1:2:3- $\text{C}_{10}\text{H}_5\text{Ph}(\text{CO})_2\text{O}$ and AlCl_3 in boiling C_6H_6 give 99% (HF gives much less) of 3:4-benzfluorenone-1-carboxylic acid and thence (basic Cu carbonate; 310–320°) 84% of 3:4-benzfluorenone. MgMeCl in $\text{Et}_2\text{O-C}_6\text{H}_6$ then gives 9-methyl-3:4-benzfluorene-9-ol (84%), m.p. 117.8–118.6°, which, when dehydrated in boiling AcOH , gives a polymeride, $(\text{C}_{18}\text{H}_{12})_x$, darkens at $\sim 200^\circ$, m.p. 275–280°, but is

converted by boiling in AcOH and then hydrogenating (PtO₂) in AcOH into 9-methyl-3:4-benzfluorene, m.p. 80.8—82° (*picrate*, m.p. 128—128.5°), and a little polymeride. M.p. are corr. R. S. C.

Polycyclic aromatic hydrocarbons. XXII. C. L. HEWETT. **XXIII.** J. W. COOK and (MRS.) A. M. ROBINSON (J.C.S., 1940, 293—303, 303—304).—XXII. Carcinogenic activity, regarded as inherent in 3:4-benzphenanthrene derivatives (cf. A., 1938, II, 132, 438), especially when further substituted in the 1- and 2-positions, is observed in 1-methyl-3:4-benzphenanthrene (I), m.p. 77—78°, b.p. 210° (bath)/0.4 mm. [*picrate* (II), m.p. 112.5—113.5°], and in 2-isopropyl-3:4-benzphenanthrene (III), m.p. 91.5—92.5° (*picrate*, m.p. 116—117°), and is shared by the analogous 1:2-dimethylchrysene (IV), m.p. 127—128° (for prep. see below). In the prep. of (I), 3:4-benz-1-phenanthroic acid (*loc. cit.*) gives, via the chloride, the anilide, m.p. 215—216°, which with PCl₅ in C₂H₅Cl₄, followed by SnCl₄—HCl—Et₂O and hydrolysis, gives 3:4-benz-1-phenanthraldehyde, m.p. 81—82°, the semicarbazone, m.p. 220—222°, of which is heated with NaOEt at 180°, and the distilled product, b.p. 200—210°/0.4 mm., converted into (II), which in C₆H₆ passed through Al₂O₃ gives (I).

In the prep. of (III), 1:2-C₁₀H₆Br·CHO, which is obtained in good yield (cf. Mayer *et al.*, A., 1922, i, 740) from 1:2-C₁₀H₆Br·CH₂Br and (CH₃)₆N₄ in boiling AcOH, with CH₂Ph·CO₂Na—Ac₂O on the water-bath gives α-phenyl-β-2-(1-bromonaphthyl)acrylic acid, m.p. 211—212°, which with KOH at 260° forms 3:4-benz-2-phenanthroic acid, m.p. 236—237° (*Na salt*). With MeOH—HCl this forms its *Me ester*, m.p. 76—77°, converted by MgMeI—Et₂O, followed by NH₄Cl and ice, into 3:4-benz-2-phenanthryldimethylcarbinol, m.p. 139—140°, which with C₆H₅(NO₂)₃·OH in boiling EtOH gives the *picrate* (V), m.p. 113—113.5°, of 2-isopropenyl-3:4-benzphenanthrene, isolated from (V) in C₆H₆ by Al₂O₃, and hydrogenated (Pd—EtOH) to (III). Prep. of 1:2-dihydro-3:4-benz-1-phenanthroic acid (VI), m.p. 140.5—141.5°, is not very satisfactory. 1:2-C₁₀H₆Br·OAc and NaOEt—Et₂O—Et₂C₂O₄ give, after 16 hr. at room temp. and 2 hr. at the b.p. followed by treatment with dil. H₂SO₄ and heating of the ethereal extract at 200—210°/20 mm., *Et 1-bromo-2-naphthylmalonate*, b.p. 187—189°/0.3 mm., of which the *Na derivative* with CH₂PhCl—EtOH, followed by boiling with KOH—EtOH, gives, after decarboxylation of the dibasic acid, α-2-(1-bromonaphthyl)-β-propionic acid (VII), m.p. 131—132° (isolated through the *Me ester*, in the fraction of b.p. 210—220°/0.4 mm.). Attempted ring-closure of (VII) by KOH in quinoline at 250—260° for 2 hr. gives α-phenyl-β-2-(1-bromonaphthyl)ethane, b.p. 210°/0.3 mm. With KOH at 260° for 15 min., (VII) gives, after fractionation of the esterified product and hydrolysis of the fractions, mainly β-phenyl-α-2-(1-hydroxynaphthyl)propionic acid, m.p. 146.5—147.5°, with small amounts of (VI) and of 3:4-benz-1-phenanthroic acid.

The prep. of (IV) is effected by two routes. (i) 2:1-C₁₀H₆Me·CH₂Cl with Zn and aq. EtOH (water-bath) gives [with as-(2:2'-dimethyl-1:1'-dinaphthyl)-ethane, m.p. 177—178°] 1:2-C₁₀H₆Me₂ (VIII), which

with Br in CS₂ gives 4-bromo-1:2-dimethylnaphthalene (IX), m.p. 39—40°, b.p. 190—195°/14 mm., isolated through the *picrate*, m.p. 108—109°. The constitution of (IX) is established by treating the Grignard derivative (X) with Me₂SO₄ and obtaining 1:2:4-C₁₀H₅Me₃. With (CH₃)₂O, (X) gives β-(3:4-dimethyl-1-naphthyl)ethyl alcohol, m.p. 65°, b.p. 150—152°/0.3 mm., of which the chloride, m.p. 44—45°, b.p. 140—145°/0.3 mm., with Mg and 2-methylcyclohexane in Et₂O gives, after treatment with ice and NH₄Cl, a carbinol, b.p. (impure) 195—200°/0.5 mm., dehydrated (P₂O₅) to a gum which resinifies when heated with Se. Chloromethylation of (VIII) by paraformaldehyde and HCl in AcOH at room temp. for 16 hr. (better than at 60° for 20 hr.) gives 3:4-dimethyl-1-chloromethylnaphthalene (XI), m.p. 70—71° (converted by Zn and aq. EtOH to 1:2:4-C₁₀H₅Me₃), with 3:4:3':4'-tetramethyl-1:1'-dinaphthylmethane, m.p. 174—175°. With aq. KCN in boiling EtOH, (XI) gives, after hydrolysis, a large proportion of a neutral substance, and 3:4-dimethyl-1-naphthylacetic acid, m.p. 181—182°, of which the pure nitrile, m.p. 66.5—67.5°, b.p. 160—170°/0.5 mm., is obtained from (XI) and Cu₂(CN)₂ in CH₂Ph·CN at 160—170° and at 220°, and of which the *Na salt* with o-NO₂-C₆H₄·CHO and Ac₂O at 130° (7 hr.) gives α-(3:4-dimethyl-1-naphthyl)-o-nitrocinnamic acid, m.p. 213—214° (*NH₄ salt*), reduced by FeSO₄—NH₃ to the o-amino-acid, m.p. 226—227° (*K salt*). The last with H₂SO₄—NaNO₂ and Cu powder, followed by heating at 70°, gives 1:2-dimethylchrysene-7-carboxylic acid, m.p. 234—235°. This is decarboxylated by Cu powder in boiling quinoline to a product which, when distilled over Na at 200°/0.5 mm., gives (IV), oxidised by Na₂Cr₂O₇—AcOH to a quinone-like substance, m.p. 157—159°. (ii) Chrysaquinone with MgMeI and Et₂O, followed by ice and NH₄Cl, gives 1:2-dihydroxy-1:2-dimethyl-1:2-dihydrochrysene (XII), m.p. 154—155°. This heated with HI—AcOH gives a bimol. product, C₄₀H₃₂ (?), m.p. 258—260°, also obtained from (XII) and aq. HI—P at 175—180°. (XII) is unchanged by HCl—CHCl₃, and in AcOH with mineral acids or I is resinified. With HCl in cooled MeOH, (XII) gives 1:2-dimethylchrysene 1:2-oxide (XIII), m.p. 155—156°, which with HI in AcOH gives an I-compound, m.p. 115°, reduced by Zn—EtOH to (IV). With H₂—Pt in AcOH at 60—70°, (XIII) gives (IV), in poor yield. With H₂—Pd in COMe₂, (XIII) gives a quant. yield of 1:2-dihydro-1:2-dimethylchrysene, m.p. 104—104.5°, readily dehydrogenated to (IV).

In an attempt to synthesise 1:2:3:4-tetramethylphenanthrene, the corresponding anthracene was obtained. 2-C₁₀H₇Pr⁺ with Br in CHCl₃ gives 2-α-bromopropionynaphthalene, m.p. 81—82°, which with CMeNa(CO₂Et)₂ in C₆H₆ (first in freezing mixture, eventually boiling) gives, after hydrolysis, decarboxylation at 190—200°, Me esterification, and hydrolysis, β-2-naphthoyl-αβ-dimethylpropionic acid, m.p. 147.5—148.5°. The *Me ester*, m.p. 79.5—80°, b.p. 180—187°/1 mm., in C₆H₆ with MgMeI—Et₂O gives, after hydrolysis and acidification, γ-2-naphthyl-αβγ-trimethylbutyrolactone, m.p. 131—131.5°. This when boiled with Zn, aq. HCl, and PhMe gives γ-2-naphthyl-αβγ-trimethylbutyric acid, m.p. 124.5—125.5° (*Na*

salt), which with 80% (vol.) H_2SO_4 (water-bath) yields 4-keto-1:2:3-trimethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 190°/0.8 mm. The carbinol arising from the last and MgMeI , when dehydrated and heated with Pd , gives a mixture which cannot be purified. 1:2:3:4-Tetramethylnaphthalene (XIV), m.p. 106.5—107.5° (picrate, m.p. 182—183°), is obtained by chloromethylation of 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ to 2:3-dimethyl-1-chloromethylnaphthalene, m.p. 86—87°, quant. reduction by Pd-H_2 in COMe_2 to 1:2:3- $\text{C}_{10}\text{H}_5\text{Me}_3$, new m.p. 27—28°, and chloromethylation to 2:3:4-trimethyl-1-chloromethylnaphthalene, m.p. 94—95°, which is hydrogenated to (XIV). In aq. HNO_3 at 175—180° (7 hr.), (XIV) gives a product converted through Ag salts and MeI into Me_6 mellitate. With succinic anhydride and AlCl_3 in PhNO_2 , (XIV) yields α -(1:2:3:4-tetramethyl-6-naphthoyl)propionic acid, m.p. 196—197°, reduced by Zn-Hg in aq. HCl and PhOMe at the b.p. to γ -1:2:3:4-tetramethylnaphthylbutyric acid, m.p. 153.5—154.5°, which with 80% (vol.) H_2SO_4 (steam-bath) gives 5-keto-1:2:3:4-tetramethyl-5:6:7:8-tetrahydroanthracene, m.p. 178—179°. The semicarbazone, m.p. >270°, of the last with NaOMe at 180° gives 1:2:3:4-tetramethyl-5:6:7:8-tetrahydroanthracene, m.p. 127.5—128°, b.p. 180—185°/0.5 mm. This with Pt at 320—330° gives 1:2:3:4-tetramethylantracene (XV), m.p. 135.5—136.5°, b.p. (crude) 200—220°/0.4 mm. (picrate, m.p. 165—166°). The structure of (XV) as an anthracene is shown by its reaction with maleic anhydride to an adduct (acid, dehydrated in xylene to the anhydride, $\text{C}_{22}\text{H}_{20}\text{O}_3$, decomp. 270—290°), which when sublimed at 300°/5 mm. regenerates (XV). With $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$, (XV) gives 1:2:3:4-tetramethylantraquinone, m.p. 232—233°, shown to have a *p*-structure by its forming a vat dye with Zn-NaOH in dioxan (but not without the solvent), and by giving no reaction with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$.

XXIII. Carcinogenic activity in 5-alkyl-1:2-benzanthracenes decreases as the alkyl chain is lengthened. 5-Keto-5:6:7:8-tetrahydro-1:2-benzanthracene with Grignard derivatives of alkyl bromides in Et_2O and C_6H_6 , followed by ice and NH_4Cl , gives *tert.* carbinols, which when dehydrated by picric acid in EtOH yield picrates of 5-alkyl-7:8-dihydro-, dehydrogenated by Pt-black at 300—310° for 24 hr. to 5-alkyl-1:2-benzanthracenes, which are purified through their picrates. The following are described (m.p. of picrates given in parentheses): 5-ethyl-, m.p. 109—110° (159—160°), 5-n-butyl-, m.p. 69—70° (124—125°), 5-n-amyl-, m.p. 59—60° (90—91°), 5-n-hexyl-, m.p. 47—48° (86—87°), and 5-n-heptyl-7:8-dihydro-1:2-benzanthracene (XVI), m.p. 53—54° [80° (dipicrate)], and 5-n-butyl-, m.p. 81° (116—117°), 5-n-amyl- (XVII), m.p. 93° (85—86°), 5-n-hexyl- (XVIII), m.p. 72—73° (90—91°), and 5-n-heptyl-1:2-benzanthracene, m.p. 68° (82—83°). A by-product, $\text{C}_{25}\text{H}_{18}$ (XIX) (structure suggested), m.p. 116.5—117.5°, is formed in the dehydrogenation of (XVI). With $\text{s-C}_6\text{H}_3(\text{NO}_2)_3$, (XVII), (XVIII), and (XIX) form complexes, m.p. 112—113°, 116—117°, and 159—160°, respectively. E. W. W.

Synthesis of 2-methyl-3:4-benzphenanthrene.
M. S. NEWMAN and L. M. JOSHEL (J. Amer. N*** (A., II.)

Chem. Soc., 1940, 62, 972—974).— $\text{CHPh}_2\cdot\text{CHO}$, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and NHEt_2 , first at room temp. and then at 100°, give after hydrolysis ($\text{H}_2\text{SO}_4\text{-AcOH-H}_2\text{O}$) and decarboxylation (200°) β -benzhydrilglutaric acid (I), m.p. 177.6—178.2° (Me_2 ester, m.p. 73.4—74.2°, b.p. $\sim 180^\circ/2$ mm.), converted by HF at room temp. into 4-keto-1-phenyl-1:2:3:4-tetrahydro-2-naphthylacetic acid (89%), m.p. 115.4—116.2° [also obtained from the anhydride of (I) by AlCl_3 in $(\text{CHCl}_2)_2$], which is reduced (Martin-Clemmensen) to 1-phenyl-1:2:3:4-tetrahydro-2-naphthylacetic acid, m.p. 140.2—140.8° (lit. 138—139°). MgMeCl in $\text{Et}_2\text{O-C}_6\text{H}_6$ and dehydrogenation by Pd-C at 290—320° then gives 2-methyl-3:4-benzphenanthrene, m.p. 70.4—71° (lit. 69.5—70°) (picrate, m.p. 141.8—143.2°). 2-Keto-1:2:9:10:11:12-hexahydro-3:4-benzphenanthrene and MgEtBr in C_6H_6 give an alcohol, which after dehydration by I and dehydrogenation by S at 230° gives 2-ethyl-3:4-benzphenanthrene, m.p. 50.4—51.2° [picrate, m.p. 78.4—80°; $\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 105.6—106.6°]. M.p. are corr.

R. S. C.

Synthesis of 1-methylchrysene and related compounds. M. S. NEWMAN (J. Amer. Chem. Soc., 1940, 62, 870—874).—Prep. of $\text{Ph}[\text{CH}_2]_2\cdot\text{CHPh}\cdot\text{CN}$ and 1-keto-1:2:3:4-tetrahydronaphthalene (I) is improved. Interaction of (I) with $\text{CHMeBr}\cdot\text{CO}_2\text{Et}\cdot\text{Zn-I}$, dehydration (I; 230°), and then hydrolysis (boiling KOH-EtOH) of the product gives α -2-phenyl-3:4-dihydro-1-naphthylpropionic acid, m.p. 210.2—210.6° (with a little *Et* α -1-hydroxy-2-phenyl-1:2:3:4-tetrahydro-1-naphthylpropionate, m.p. 90.4—91.4°), reduced by $\text{H}_2\text{-Cu-Ba}$ chromite in dioxan at 200°/127 atm. to α -1-phenyl-1:2:3:4-tetrahydro-1-naphthylacetic acid, m.p. 143—148° (147.6—148.8°). $\text{PCl}_5\text{-C}_6\text{H}_6$ and then $\text{AlCl}_3\text{-C}_6\text{H}_6$ at room temp. and later 50° give 2-keto-1-methyl-1:2:7:8:1a:7a-hexahydrochrysene (II), which by reduction [$\text{Al}(\text{OPr}^i)_3\text{-Pr}^i\text{OH}$], dehydration (I; 230°), and dehydrogenation (S; 240—250°) gives 1-methylchrysene (III) (36%), m.p. 117.2—117.8° [picrate, m.p. 142.6—143°; $\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 172.6—173.6°]. Treatment of (II) with $\text{MgMeBr-Et}_2\text{O-C}_6\text{H}_6$, heating at 220°/vac., and dehydrogenation (S; 230—240°) gives 1:2-dimethylchrysene, dimorphic, m.p. 128.6—129.8° [picrate, m.p. 134.4—135.4° (decomp.); $\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 158.6—159.4°], and some (III). Reactions starting from (I) and $\text{CHEtBr}\cdot\text{CO}_2\text{Et}$ give α -2-phenyl-3:4-dihydro-1-naphthyl-n-butyric acid, m.p. 156—159° (with 15% of $\text{Pr}^i\text{CO}_2\text{Et}$), and 1-ethylchrysene, m.p. 91.4—92.4° [picrate, m.p. 99.2—100.6°; $\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 125.2—125.8°], intermediates being oils. 2-Methylchrysene is slightly carcinogenic. M.p. are corr. R. S. C.

Physiologically active amines. III. *sec.* and *tert.* β -Phenylpropylamines and β -phenylisopropylamines. E. H. WOODRUFF, J. P. LAMBOOY, and W. E. BURT (J. Amer. Chem. Soc., 1940, 62, 922—924; cf. A., 1938, II, 271).—The following are prepared by (a) heating $\text{CHPh}\cdot\text{NR}$ with R'I to give $\text{CHPh}\cdot\text{NRR'I}$ and then hydrolysing with hot MeOH or EtOH , or (b) hydrogenating (Raney Ni ; 3 atm.; EtOH) $\text{RCHO-NH}_2\text{R'-NaOAc}$ or $\text{CHR}\cdot\text{NR'}$ (CH_2O gives NR'Me_2 , but other aldehydes give mixed *sec.*

and *tert.* amines). Figures in brackets are m.p. of the *hydrochlorides*. β -*Phenyl*-, b.p. 78—80°/6 mm. [135—136°], β -*o*-, b.p. 100—102°/6 mm. [137—138°], β -*m*-, b.p. 135—137°/18 mm. [142—143°], and β -*p-anisyl-isopropylmethylamine*, b.p. 117—119°/8 mm. [178.5—179.5°], β -*phenyl*-, b.p. 96—98°/18 mm. [148—159°], β -*o*-, b.p. 115—117°/8 mm. [199—200°], and β -*p-anisyl-propylmethylamine*, b.p. 127—128°/8 mm. [166.5—167.5°], β -*o*-, b.p. 104°/6 mm. [158—159°], β -*m*-, b.p. 140°/17 mm. [123—124°], and β -*p-anisylisopropylethylamine*, b.p. 137°/9 mm. [156—157°], β -*phenyl*-, b.p. 127°/30 mm. [159—160°], and β -*p-anisyl-propylethylamine*, b.p. 137°/9 mm. [156—157°], β -*phenyl*-, b.p. 100°/12 mm. [159—161°], β -*o*-, b.p. 125°/10 mm. [157—158°], β -*m*-, b.p. 132°/10 mm. [134—135°], and β -*p-anisyl-isopropyldimethylamine*, b.p. 137°/13 mm. [161—162°], β -*m*-, b.p. 130°/12 mm. [175—176°], and β -*p-anisylpropyldimethylamine*, b.p. 129°/11 mm. [198—199°], methylephedrine, m.p. 86.5—87.5° [190—191°], β -*phenyl*-, b.p. 178°/13 mm. [198—199°], β -*o*-, b.p. 194°/9 mm. [130—131°], and β -*m-anisyl-isopropylbenzylamine*, b.p. 196°/10 mm. [143—144°], β -*o*-, b.p. 197°/10 mm. [dimorphic, m.p. 146—147° and 161—162°], β -*m*-, b.p. 181°/10 mm. [148—149°], and β -*p-anisylpropylbenzylamine*, b.p. 209—212°/13 mm. [154°]. R. S. C.

Preparation and properties of 6-halogeno-carvacrylamines from *p*-cymene. R. W. BOST and G. C. KYKER (J. Amer. Chem. Soc., 1940, 62, 913—917).—Addition of 6:1:4:2- $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{MePr}^{\beta}\cdot\text{N}_2\text{Cl}$ to $\text{CuCl}\cdot\text{HCl}$ at 0° and heating at 60° gives 2-chloro-6-nitro-*p*-cymene (Me = 1) (I) (77.5%), b.p. 132—133°/2 mm., and some 2-nitro-6-hydroxy-(?5)-6'-nitrocarvacrylazo-*p*-cymene, m.p. 186—187°. Mossy Sn, conc. HCl, and EtOH reduce (I) to 6-chlorocarvacrylamine (II), b.p. 134—136°/1 mm. [hydrochloride, softens at 210—220°, m.p. 225—226° (decomp.); hydrobromide, m.p. 231—232°; nitrate, m.p. 153°; oxalate, m.p. 155°; di-, m.p. 92—93°, and tri-chloroacetate, m.p. 157°; 2:4:6-tri-, m.p. 161°, and 3:5-di-nitrobenzoate, m.p. 133—134°; picrate, m.p. 151°; *H* sulphate, m.p. 166°; benzene-, m.p. 184°, and *p*-toluene-sulphonate, m.p. 193—194°; Ac, m.p. 117—118°, Bz, m.p. 139°, 3:5-dinitrobenzoyl, m.p. 197—198°, PhSO_2 , m.p. 117.5°, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$, m.p. 115.5°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2$, m.p. 131.5°, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2$, m.p. 129.5°, and picryl derivative, m.p. 150.5—151.5°], which yields 6-chloro-2-carbamido-*p*-cymene, m.p. 180—182° (decomp.; slow heating), 185—187° (decomp.; preheated to 160°), and as hydrochloride with aq. NaNO_2 at 0° gives 6:6'-dichloro-2:2'-diazamino-*p*-cymene, m.p. 110°. Diazotisation of (II) and coupling gives azo-dyes, (m.p. as given) with β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$, m.p. 202°, PhOH, m.p. 192—193°, *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, m.p. 233°, phloroglucinol, m.p. 278°, and 1:8:3:6-(OH) $_4\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2$, m.p. >300°. 6-Bromo-, m.p. 213—214° (decomp.), and 6-iodo-carvacrylamine hydrochloride, m.p. 244—245° (decomp.), are prepared as for (II). R. S. C.

Action of amines on 9-bromo-2-nitrofluorene. New and very sensitive colour reaction for pyridine. A. NOVELLI (Rev. Fac. Cienc. Quím. La Plata, 1939, 14, 137—140).—9-Bromo-2-nitrofluorene (I) with NHEt_2 in EtOH gives 2:2'-dinitro-

bisdiphenylene-ethylene, but the appropriate NH_2Ar affords 2-nitro-9-phenyl-, m.p. 164°, -9-*p*-tolyl-, m.p. 146—147°, -9-*p*-nitrophenyl-, m.p. 222—224° (decomp.), and -9-2'-fluorenyl-fluorenylamine, m.p. 186—187°. (I) heated with $\text{C}_5\text{H}_5\text{N}$ or its derivatives and then diluted with H_2O and EtOH or COMe_2 , with subsequent addition of aq. NH_3 , gives an intense blue colour.

F. R. G.

Constitution of sulphon-amides and -anilides. A. BARONI (R.C. Atti Accad. Ital., 1939, [vii], 1, 46—49).—The parachors of 21 sulphon-amides and -anilides show that these have normal structures at 200°. In solution irregular deviations in $[P]$ are observed.

E. W. W.

Derivatives of sulphanilamide.—See B., 1940, 403, 404.

Sulphonamide derivatives of arylcarbamides. E. H. COX (J. Amer. Chem. Soc., 1940, 62, 743—744).— $\text{NHAr}\cdot\text{CO}\cdot\text{NH}_2$ (A) and ClSO_3H at 0—10° give $\text{NHAr}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ etc. (difficult to purify). $\text{NHAr}\cdot\text{CO}\cdot\text{NHAc}$ [prep. from (A) by $\text{AcCl}\cdot\text{C}_5\text{H}_5\text{N}$ at -10°, then 30°] and ClSO_3H at 50° give $\text{NHAc}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ etc. The chloride is converted by 28% NH_3 or 30% NHEt_2 at 100° into the amide. Thus are obtained *p*-*N'*-acetylcarbamido-benzene-, m.p. 192—193°, -*o*-, m.p. 197—199°, and -*m*-toluene-sulphonyl chloride, m.p. 199—201°, *p*-carbamido-benzene-, m.p. 206—207° (Ac derivative, m.p. 246—247°), -*o*-, m.p. 223—225° (Ac derivative, m.p. 231—233°), and -*m*-toluene-sulphonamide, m.p. 209—210° (Ac derivative, m.p. 226—227°), *p*-carbamido-benzene-, m.p. 148—149°, -*o*-, m.p. 165—167°, and -*m*-toluene-sulphondiethylamide, m.p. 147—148°.

R. S. C.

Action of amines on semicarbazones. A. B. CRAWFORD (J. Roy. Tech. Coll., 1940, 4, 607—616).— $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ (I) at 160° give NH_3 , *p*-isopropylidenesemicarbazidoazobenzene (II) (12—15%), m.p. 210°, and $(\text{NMe}_2)_2$ with some $(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$. HCl in hot, aq. EtOH hydrolyses (II) to *p*-8-semicarbazidoazobenzene (III), *p*- $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$, m.p. 237° (decomp.; red at ~210°) [hydrochloride, m.p. ~209° (decomp.), colour variable; *CHPh* derivative, m.p. 217—218°]. Absorption spectra of (I) and (III) in EtOH and aq. HCl are in part correlated with structure.

R. S. C.

Metallic complexes of *o*-substituted azo-dyes. J. L. BOYLE, W. M. CUMMING, and A. B. STEVEN (J. Roy. Tech. Coll., 1940, 4, 617—632).—*o*- NH_2 , *o*- CO_2H , and *o*-Oalk can take part in metal-lake formation of azo-dyes. The following lakes are prepared from pure intermediates. $1\text{Cu}:1\text{dye}$ compounds with *p*- $\text{C}_6\text{H}_4\text{R}\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (R = NO_2 or SO_3H), $\text{NH}_2\text{Ph} \rightarrow 6:2\text{-SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, $2:5:1\text{-OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (I), $2:5:1\text{-OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}_2 \rightarrow 5:1\text{-SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ (II), and *o*- $\text{C}_6\text{H}_4\text{R}\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (R = OMe or CO_2H); $1\text{Cu}:2(1:2\text{-PhN}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH})$; $?4\text{Cu}:3[5:2:1\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}]$; $3\text{Cu}:2\text{dye}$ compounds with $2:5:1\text{-OH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}_2 \rightarrow 6:2\text{-SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ (III), $4:1:2:6\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2 \rightarrow m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (IV), and $4:1:2\text{-NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2 \rightarrow 4:1:3\text{-}$

$\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ (V); $2\text{Cu} : 1[\text{o}-\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \rightarrow 2 : 3 : 6\text{-OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2]$; $1\text{Cr} : 1\text{dye}$ compounds with $5 : 2 : 1\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, $\text{o}-\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, $\text{o}-\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \rightarrow 2 : 3 : 6\text{-OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$, and (V); $2\text{Cr} : 3\text{dye}$ compounds with (I), (II), (IV), and $\text{o}-\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \rightarrow \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$; $4\text{Cr} : 3(\text{III})$. Formulæ are ascribed.

R. S. C.

Aromatic aminohydrazines.—See B., 1940, 345.

Nuclear methylation of phenol. T. KENNEDY (Chem. and Ind., 1940, 297).— $4 : 1 : 3 : 5\text{-OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CH}_2\cdot\text{OH})_2$, prepared from *p*-cresol by CH_2O in aq. alkali, is hydrogenated (Cu chromite; dioxan) to mesitol, similarly obtained starting from a commercial mixed cresol.

R. S. C.

Deepening of colour of sodium nitrophenoxide solutions with elevation of temperature. T. L. DAVIS and J. L. RICHMOND (J. Amer. Chem. Soc., 1940, 62, 756—761).—The thermotropic colour intensification and its retardation by Na_2CO_3 are similar for aq. *o*-, *m*-, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{ONa}$, the *m*-compound being somewhat less affected. The Na salts may be

formed by addition of NaOH to give $\text{CH}:\text{CH}\cdot\text{C}(\text{OH})_2$
(and its *p*-analogue) and $\text{CH}(\text{OH})\cdot\text{C}(\text{OH})_2\text{CH}$
 $\text{CH}:\text{CH}\text{---}\text{C}:\text{NO}\cdot\text{ONa}$.
The colour is due to resonance of the ions.

R. S. C.

Syntheses of stilbene derivatives. I. New synthesis of *trans*-4 : 4'-dihydroxy- $\alpha\beta$ -diethylstilbene. S. KUWADA and Y. SASAGAWA (J. Pharm. Soc. Japan, 1940, 60, 27—29; cf. Dodds *et al.*, A., 1939, II, 312).—Anisoin is converted by MgEtBr into $\alpha\beta$ -dianisylbutane- $\alpha\beta$ -diol, m.p. $113\cdot5^\circ$, transformed by short treatment with warm 50% H_2SO_4 into $\alpha\beta$ -dianisylbutan- α -one (I), b.p. $198\text{—}199^\circ/1\text{ mm.}$ (oxime, m.p. 111°), whereas conc. H_2SO_4 yields much resinous matter. (I) and MgEtBr give a material from which a homogeneous cryst. product could not be extracted but which is dehydrated by PBr_3 in CHCl_3 to 4 : 4'-dimethoxy- $\alpha\beta$ -diethylstilbene, m.p. $123\text{—}124^\circ$. This is demethylated (Späth) to *trans*-4 : 4'-dihydroxy- $\alpha\beta$ -diethylstilbene, m.p. $168\cdot5^\circ$, the absorption curve of which is closely similar to that of *trans*- $\alpha\beta$ -dimethylstilbene.

H. W.

Structure of cannabidiol. II. Absorption spectra compared with those of various dihydric phenols. R. ADAMS, C. K. CAIN, and H. WOLFF. **III. Reduction and cleavage.** R. ADAMS, M. HUNT, and J. H. CLARK (J. Amer. Chem. Soc., 1940, 62, 732—734, 735—737; cf. A., 1940, II, 80).—II. Comparison of absorption spectra of *o*- and *m*- $\text{C}_6\text{H}_4(\text{OR})_2$, $4 : 1 : 2\text{-}$ and $5 : 1 : 3\text{-C}_6\text{H}_3\text{Me}(\text{OR})_2$, $4 : 1 : 2\text{-}$ and $5 : 1 : 3\text{-n-C}_5\text{H}_{11}\cdot\text{C}_6\text{H}_2(\text{OR})_2$ (R = H or Me), cannabidiol (I) and its Me_2 ether indicates a resorcinol structure for (I). 4-*n*-Amylpyrocatechol Me_2 ether, b.p. $124\text{—}126^\circ/4\text{—}5\text{ mm.}$, is prepared from the phenol by Me_2SO_4 and 10% NaOH-EtOH .

III. (I) is probably 4- or 2-dihydro-3'-*p*-cymyl-5-*n*-amylresorcinol (Me = 1'). Hydrogenation (PtO_2 ; 2—3 atm.; AcOH) of (I) gives tetrahydrocannabidiol, b.p. $188\text{—}190^\circ/2\cdot5\text{ mm.}$, oxidised by KMnO_4 in COMe_2 to *p*-menthane-3-carboxylic acid (Me = 1) [anilide, m.p. $152\text{—}152\cdot5^\circ$ (corr.) (lit. $148\cdot5^\circ$)]. De-

hydrogenation of (I) gives oils, probably containing a Ph_2 derivative. In $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ at $210\text{—}230^\circ$ (much less well, $\text{NH}_2\cdot\text{SO}_3\text{H}$), (I) gives *p*-cymene and olivetol, b.p. (anhyd.) $170\text{—}175^\circ/2\text{ mm.}$, m.p. ($+\text{H}_2\text{O}$) 41° [*bis*-3 : 5-dinitrobenzoate, m.p. $127\text{—}128^\circ$ (corr.)].

R. S. C.

Claisen rearrangement. II. Kinetic study of rearrangement of 2 : 6-dimethylphenyl allyl ether in diphenyl ether solution. D. S. TARBELL and J. F. KINCAID (J. Amer. Chem. Soc., 1940, 62, 728—731; cf. A., 1940, I, 30).—*m*-2-Xylenol and $\text{CH}_3\text{CH}\cdot\text{CH}_2\text{Br}$ with hot NaOEt-EtOH give 85 and 15% or with Na in C_6H_6 give 55 and 45% of the allyl ether (I), b.p. $67\text{—}68^\circ/2\text{ mm.}$, and 2 : 6-dimethyl-4-allylphenol (II), b.p. $90\cdot5\text{—}91\cdot4^\circ/2\text{ mm.}$ (phenylurethane, m.p. $141\text{—}142\cdot5^\circ$, obtained by PhNCO and dry HCl), respectively. At $171\cdot6^\circ$ in absence of air (I) gives 95% of (II) and 5% of a polymeride. In Ph_2O at $185\cdot8^\circ$, $171\cdot6^\circ$, or $156\cdot9^\circ$, or alone at $171\cdot6^\circ$ or $185\cdot8^\circ$, the rearrangement is of the first order, in agreement with findings that 10% of NPhMe_2 in Ph_2O increases the velocity by only ~15% (thus excluding a prototropic change as the slow step) and that 1 or 2% of AcOH increases it by 28 or 42%, respectively. *k* increases as the reaction proceeds with the more conc. solutions. The entropy of activation is $-10\cdot1\text{ e.u.}$ at $171\cdot6^\circ$, comparison of which with that for $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ ($-9\cdot5$ under comparable conditions) indicates that rearrangement to the *o*- and *p*-positions has the same slow step. This is difficult to reconcile with chemical evidence for the cyclic mechanism, which also on Fisher-Hirschfelder models is impossible for the *p*-migration.

R. S. C.

N-Substituted aminophenols.—See B., 1940, 345.

Alkylation of *o*-hydroxyazo-compounds and anomalous reduction of the ethers obtained. (SIGNA.) E. GHIGI (Gazzetta, 1940, 70, 202—211, and Helv. Chim. Acta, 1940, 23, 428—430).—The view of Fierz-David *et al.* (A., 1938, II, 317) that the OH of *o*-hydroxyazo-compounds cannot be alkylated is incorrect. $2 : 1\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{NPh}$ (I) is converted into the Me ether (II) (cf. Charrier *et al.*, A., 1912, i, 812), which with $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH in boiling EtOH gives 2-anilino-1-naphthylamine (III), m.p. $136\text{—}137^\circ$, converted by AcOH-NaNO_2 into 3-phenyl- $\alpha\beta$ -naphthatriazole (cf. Charrier *et al.*, A., 1926, 848). PhCHO converts (III) into diphenylnaphthiminazole. With PhN_2Cl , (III) gives tarry products. With Et_2SO_4 in boiling 30% NaOH , (I) gives its Et ether, m.p. 79° , converted by $\text{Na}_2\text{S}_2\text{O}_4$ into (III). No definite products are obtained from (II) and Zn-AcOH . The acetate of (I) is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to $1 : 2\text{-NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$. $4 : 1 : 3\text{-OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\text{Ph}$ with $\text{Me}_2\text{SO}_4\text{-NaOH}$ gives its Me ether, m.p. $53\text{—}54^\circ$, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 6-methoxy-3-methylhydrazobenzene, m.p. $91\text{—}92^\circ$ (Ac_1 derivative, m.p. $124\text{—}125^\circ$), which with boiling 10% H_2SO_4 gives 5-methoxy-2-methylbenzidine, m.p. $86\text{—}87^\circ$ [sulphate, m.p. $\sim 300^\circ$; Ac_4 derivative, m.p. $188\text{—}189^\circ$].

E. W. W.

[Interaction of] styrene and organic disulphides [in presence of] iodine. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1939, 13, B, No. 14, 6 pp.).—

R_2S_2 and $CHPh:CH_2$ (I) in presence of a little I (in C_6H_6 or other solvent, if solid) give $\alpha\beta$ -di-methyl- (II), b.p. 149—150°/10 mm., -ethyl-, b.p. 163—164°/11 mm., -(carbethoxyethyl)-, b.p. 210—212°/3 mm., and -phenyl-, m.p. 57—58°, -thioethylbenzene, $SR \cdot CHPh \cdot CH_2 \cdot SR$. Analogous condensations with other unsaturated components and of (I) with tetra- and tri-thioglycolic acid, $(CO_2H \cdot CH_2 \cdot S)_2S$ (prep. from $SH \cdot CH_2 \cdot CO_2H$ by SCl_2), m.p. 122—124°, failed. Perhydrol and (II) in $COMe_2$ give the derived di-sulphoxide, forms, m.p. 122—124° (clear at 126°) and 130—131°.

R. S. C.

Derivatives of 4 : 4'-diaminodiphenyl sulphide.
—See B., 1940, 345.

Synthesis of sulphur-containing chemotherapeutic products. I. *p*-Nitrophenyl *p*-aminophenyl sulphoxide and sulphone. J. O. GABEL and F. L. GRINBERG. II. *p*-Nitrophenyl *p*-acetamidophenyl sulphide. J. O. GABEL and A. L. SCHAFANION (J. Appl. Chem. Russ., 1939, 12, 1481—1484, 1485—1489).—I. 4-Nitro-4'-acetamidodiphenyl sulphide (I) in $AcOH$ and H_2O_2 (24 hr. at room temp., then 30 min. at 100°) give the sulphoxide (II), m.p. 210—211°, in 90% yield; when the final heating is prolonged to 3—3.5 hr. the product is the sulphone (III), m.p. 219—220° (yield 90—96%). (II) and (III) are hydrolysed (boiling 18% HCl) to 4-nitro-4'-aminodiphenyl sulphoxide, m.p. 132—134°, and sulphone, m.p. 167—169°, respectively.

II. Na_2S and $p\text{-}C_6H_4Cl \cdot NO_2$ in $EtOH$ (at the b.p.) yield a mixture of $(p\text{-}NO_2 \cdot C_6H_4)_2S$ and $p\text{-}NO_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot NH_2$. *p*- $NHAc \cdot C_6H_4 \cdot SO_2Cl$ is reduced. (Zn and aq. $EtOH \cdot HCl$ at 0° until evolution of H_2 ceases, then 25 min. at 100°) to *p*- $NHAc \cdot C_6H_4 \cdot SH$, which with $p\text{-}C_6H_4Cl \cdot NO_2$ in $EtOH \cdot NaOH$ gives (I) in good yield.

R. T.

Reversibility of the rearrangement of *o*-hydroxysulphones. R. R. COATS and D. T. GIBSON (J.C.S., 1940, 442—446).—Rearrangement (A) of *o*-hydroxysulphones to sulphino-ethers (cf. McClement *et al.*, A., 1937, II, 337) is reversible; the reverse change is much slower, but roughly of the same order. *o*-Nitrophenyl 1-sulphino-2-naphthyl ether, m.p. 116°, in aq. $NaOAc$ at 50° for 5 hr. is converted (almost quant.) into *o*-nitrophenyl 2-hydroxy-1-naphthyl sulphone, m.p. 180—181° (2 forms) (cf. Levy *et al.*, A., 1932, 156); the conversion occurs in aq. $COMe_2$ and partly even in dry Et_2O -ligroin. 4'-Chloro-2-nitro-3' : 5'-dimethyl-, new m.p. 131°, 2-nitro-4' : 6'-dimethyl-, m.p. 153° (lit. 129°), 2-nitro-4'-methyl-, new m.p. 134°, and 6'-chloro-2-nitro-4'-methyl-2'-sulphinodiphenyl ether, m.p. 170°, rearrange to 5'-chloro-2-nitro-2'-hydroxy-4' : 6'-dimethyl-, 2-nitro-2'-hydroxy-3' : 5'-dimethyl-, 2-nitro-2'-hydroxy-5'-methyl-, and 3'-chloro-2-nitro-2'-hydroxy-5'-methyl-diphenyl sulphone respectively; the times for attaining equilibrium at the most favourable p_H in $\sim N/150$ solution at $50 \pm 2^\circ$ are 5, 250, 400, and 450 hr., respectively. Conversion of 2 : 4-dinitrophenyl 3-sulphino-*p*-tolyl ether, m.p. 140° (decomp.) (lit. 117—118°), into 2 : 4-dinitro-2'-hydroxy-5'-methylidiphenyl sulphone is rapid (2 hr.). Inter-conversion in either direction is facilitated by the positive character of the C atom *o* to NO_2 and attached

to SO_2 (in the sulphone). The rate of conversion of 2-nitro-4'-hydroxy-2'-sulphinodiphenyl ether (*monohydrate*, 2 forms, m.p. 98°; not dehydrated by P_2O_5 ; cf. Kent *et al.*, A., 1934, 647) could not be determined, owing to the solubility of 2-nitro-2' : 5'-dihydroxydiphenyl sulphone. Although *o*-nitrophenyl β -hydroxyethyl sulphone almost instantaneously gives β -*o*-nitrophenoxymethanesulphonic acid, new m.p. 124°, and 2-nitro-2'-hydroxy-5'-methoxydiphenyl sulphone affords 2-nitro-4'-methoxy-2'-sulphinodiphenyl ether, new m.p. 128°, no reverse reaction was obtained in either case. Theoretical aspects are discussed. The conversion medium may be $NaOAc$, HCO_2Na , or aq. $COMe_2$. The relative strengths of $PhSO_2H$ and *o*- and *p*- $C_6H_4Me \cdot SO_2H$ are given. Rearrangement (A) occurs even in aq. NH_3 , where co-ordination is impossible (cf. Heppenstall *et al.*, A., 1938, II, 320).

A. T. P.

Condensation of phenol and ethylene oxide. R. A. SMITH (J. Amer. Chem. Soc., 1940, 62, 994).— $OH \cdot [CH_2]_2 \cdot OPh$, b.p. 165°/80 mm., is best (94%) prepared from $PhOH$ and $(CH_2)_2O$ in H_2 at 200°/2500 lb.

R. S. C.

Decomposition of chlorosulphinic esters. M. P. BALFE and J. KENYON (J.C.S., 1940, 463—464; cf. A., 1930, 598).—Aspects of the decomp. of semi-aromatic chlorosulphinates are reviewed (cf. Gerrard, A., 1940, II, 127). In presence of Cl^- , derived either from the hydrochloride of *tert.* bases or by formation of the unstable intermediate additive compound, the chloride RCl is formed with inversion of configuration. In absence of *tert.* base, the chloride is formed with retention of configuration, probably by the intramol. mechanism suggested by Hughes *et al.* (A., 1937, II, 363).

A. T. P.

Formation of phenol-formaldehyde resins. I. Condensation of guaiacol and formaldehyde. H. VON EULER, E. ADLER, and D. FRIEDMANN (Arkiv Kemi, Min., Geol., 1939, 13, B, No. 12, 7 pp.).—Guaiacol (I) (2.2 mols.), 40% aq. CH_2O (1 mol.), and a little HCl at 100° give (? 4 : 4') (II), m.p. 107—108°, and (? 4 : 2')-dihydroxy-3 : 3'-dimethoxydiphenylmethane, m.p. 119—120°. 40% CH_2O (2 mols.), (I) (1 mol.), and 10% $NaOH$ (1 mol.) at room temp. give a mixture of alcohols, probably 1 : 2 : 4- $OH \cdot C_6H_3(OMe) \cdot CH_2 \cdot OH$ and 1 : 4 : 6 : 2- $OH \cdot C_6H_2(CH_2 \cdot OH)_2 \cdot OMe$, and a little [4 : 3 : 5 : 1- $OH \cdot C_6H_2(OMe)(CH_2 \cdot OH)_2 \cdot CH_2$, m.p. 148—149° (lit. 146.5—147°) [also obtained from (II) by CH_2O (2 mols.) and $NaOH$ (2 mols.) at 40—50°].

R. S. C.

Steric course of dimerising reductions. N. A. SÖRENSEN, J. STENE, and E. SAMUELSEN (Annalen, 1940, 543, 132—142).—Reduction (method : Kuhn *et al.*, A., 1928, 281) of $CHPh:CH \cdot CHO$ gives approx. equal amounts of *meso*- (I), m.p. 156° (dibenzoate, m.p. 173—174°), and *r*-hydrocinnamoin (II), m.p. 107.5° (corr.); the reaction mixture is freed from (I) and the residual syrup treated with $BzCl$ in C_5H_5N at 0°, whereby the *dibenzoate* (III), m.p. 165.5° (corr.), of (II) is formed. Hydrolysis ($EtOH \cdot NaOH$) of (III) affords (II) whilst oxidation (O_3 in $AcOH$) gives $PhCHO$ (1.6 mols.) and *r*-dibenzoyltartaric acid (+2 H_2O), m.p. 112—114° resolidifying at 116—120° with m.p. 168—170°, m.p. (anhyd.) 174—175° (cf.

lit.) [anhydride, m.p. 175—177° (corr.)]. Contrary to Thiele (A., 1899, i, 616; cf. Farmer *et al.*, A., 1928, 151), distillation of (I) at atm. pressure gives p - $C_6H_4Ph_2$; reaction is considered to occur thus: (I) $\rightarrow [2CHPh:CH:CH:OH \leftrightarrow 2OH:CH:CH:CHPh] \rightarrow CHPh:CH:CH(OH):CHPh:CH:CH:OH \rightarrow p-C_6H_4Ph_2$. Dimerising reductions of $CHR:CH:CHO$ with Zn, Zn-Cu, Al-Hg, VSO_4 , etc. are considered to give $CHR:CH:CH:OH$, which can dimerise (to the glycol) or rearrange (cf. above). H. B.

Ring-enlargement in the hydroaromatic series.

I. Experiments with 3:3:5-trimethylcyclohexylmethylamine (dihydroisophorylmethylamine). H. BARBIER (Helv. Chim. Acta, 1940, 23, 519—524).—*iso*Phorone is scarcely affected by $CH_2Cl:CO_2Et$ and NaOMe whereas dihydroisophorone (I) yields *Et* 3:3:5-trimethylcyclohexylglycidate, b.p. 105°/4 mm., in 70% yield. This is converted by hydrolysis followed by distillation of the acid under diminished pressure into 3:3:5-trimethylcyclohexanecarbaldehyde, b.p. 53°/4 mm., 201° (corr.)/730 mm. (semicarbazone, m.p. 132°). The corresponding oxime, b.p. 98°/4 mm., is dehydrated by boiling Ac_2O to the nitrile, b.p. 73°/4 mm., 226° (corr.)/730 mm., which is reduced (Na in boiling EtOH) to 3:3:5-trimethylcyclohexylmethylamine, b.p. 58°/4 mm., 202° (corr.)/728 mm. (hydrochloride, m.p. 245—250°). This is deaminated ($NaNO_2$ in dil. AcOH) to 1:1:3-trimethylcycloheptene, b.p. 38°/4 mm., 152° (corr.)/732 mm., 1:3:3:5-tetramethylcyclohexanol, b.p. 65°/4 mm., 185° (corr.)/729 mm., m.p. 82° [also obtained from (I) and $MgMeI$ and dehydrated by p - $C_6H_4Me:SO_3H$ to tetramethylcyclohexene, b.p. 149.5° (corr.)/721 mm.], and a mixture of trimethylcycloheptanols which is oxidised and treated with $NH_2:CO:NH:NH_2$, thus leading to a homogeneous 3:5:5- or 3:3:5-trimethylcycloheptanone, b.p. 62°/4 mm. (semicarbazone, m.p. 174°), also obtained directly from (I) and CH_2N_2 . H. W.

Ring-enlargement in the hydroaromatic series.

II. Experiments with 2:2:6-trimethylcyclohexylmethylamine (dihydrocyclogeranylmethylamine). H. BARBIER (Helv. Chim. Acta, 1940, 23, 524—532).—*cyclo*Gernanonitrile is reduced (Raney Ni in PhMe at 110°/30—50 atm.) to a mixture of 2:2:6-trimethylcyclohexylmethylamines (I), b.p. 62°/4 mm., 212.5° (corr.)/732 mm. [hydrochloride; mercurichloride, m.p. 215°; platinichloride, m.p. 287° (decomp.)], and (II), b.p. 210.2° (corr.)/724 mm. [hydrochloride; mercurichloride, m.p. 161°; platinichloride, m.p. 265° (decomp.)], and (?) *di*(dihydrocyclogeranylmethylamine), b.p. 160°/4 mm. Deamination of (I) leads to 1:1:4-trimethyl- Δ^3 -cycloheptene (III), b.p. 35°/4 mm., 165.5° (corr.)/732 mm., 2:2:6-trimethylcyclohexylmethyl alcohol (IV), b.p. 81°/4 mm. (allophanate, m.p. 172°), and a mixture of trimethylcycloheptanols (V). (IV) is characterised by successive conversions into dihydrocyclocitral, b.p. 62°/4 mm. (semicarbazone, m.p. 185°), and dihydrocyclogeranic acid, m.p. 82°. (II) yields a cyclocitronellol, b.p. 85°/4 mm. (allophanate, m.p. 132°). (V) is oxidised to a mixture from which is obtained 2:2:6- or 3:3:7-trimethylcycloheptanone, b.p. 58°/4 mm., 207°/733 mm. (semicarbazone, m.p. 190—192°); this is transformed by

$CH_2Cl:CO_2Et$ and NaOMe in C_6H_6 into the glycidic ester, b.p. 115°/4 mm., which gives 2:2:6- or 3:3:7-trimethylcycloheptanecarbaldehyde, b.p. 65—67°/4 mm. (semicarbazone, m.p. 121°). 2:5:5-Trimethyl- Δ^2 -cycloheptenone, b.p. 66—68°/4 mm. (semicarbazone, m.p. 195—196°), obtained by the action of SeO_2 on (III), gives a glycidic ester, b.p. 124°/4 mm., which is transformed into (probably) 2:5:5-trimethyl- Δ^2 -cycloheptenecarbaldehyde, b.p. 72°/4 mm. (semicarbazone, m.p. 194°). H. W.

Reduction of 7-hydroxy-4-keto-1:2:3:4-tetrahydrophenanthrene with sodium and amyl alcohol. M. MIYASAKA (J. Pharm. Soc. Japan, 1939, 59, 278—282).— γ -(6-Methoxy-2-naphthyl)-butyric acid, m.p. 135°, and $P_2O_5-C_6H_6$ give 4-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 56° (semicarbazone, m.p. 235°), converted by $AlCl_3$ or $AlBr_3$ in C_6H_6 into the 7-hydroxy-4-keto-compound (I), m.p. 188° (benzoate, m.p. 155°), which with $Na-C_5H_{11}:OH$ gives (probably) trans, m.p. 189°, and cis-4:7-dihydroxy-1:2:3:4:9:10:11:12-octahydrophenanthrene, m.p. 177° (7-benzoate, m.p. 111°; 3:5-dinitrobenzoate, m.p. 198°). (I) and H_2 (PtO_2 in AcOH) give 2-hydroxy-1:2:3:4:5:6:7:8-octahydrophenanthrene (3:5-dinitrobenzoate, m.p. 157°). 4-Hydroxy-7-methoxy-1:2:3:4-tetrahydro-, m.p. 117° (acetate, m.p. 105°), and -1:2:3:4:9:10:11:12-octahydro-, m.p. 107°, and 2-hydroxy-5:6:7:8-tetrahydro-phenanthrene, m.p. 132° (picrate, m.p. 183°), are prepared. A. T. P.

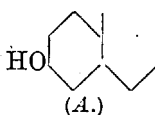
Preparation of amino-alcohols.—See B., 1940, 345.

Speculation regarding the ring structure of sterols and related substances. (SIR) R. ROBINSON (J.C.S., 1940, 509—510).—It is doubtful whether the isoprene hypothesis can be applied to sterols. It is more probable that two identical progenitors (cf. A) together with a component introducing a side-chain combine to form different members of the group. It is suggested that group (A) may originate from tyrosine (I) or a protein containing (I) residues. [(By E. WALKER.) The unfavourable effect of (I) on formation of ergosterol by yeast is noted.] CH_2O (or its equiv.) may be the methylating agent. C-methylation and group migration are discussed and a structural scheme is suggested. It is possible to postulate the formation of the precursor suggested by Marker (A., 1938, II, 415). A. T. P.

Steroid alcohols.—See B., 1940, 405.

Hydrolysis of dicholesteryl ether by acid clay. T. KAWASAKI (J. Pharm. Soc. Japan, 1939, 59, 268—270; cf. A., 1940, II, 75).—Dehydration of cholesterol (I) by acid clay to dicholesteryl ether (II) is never complete, since (II) is similarly converted in C_6H_6 or CCl_4 into ~8% of (I). Yoder's conclusion (A., 1937, II, 16) that cholesterylenesulphonic acid is formed from (I) and floridin is erroneous. A. T. P.

Photochemical process in the formation of photopyrocalfiferols. A. WINDAUS, K. DIMROTH, and W. BREYWISCH (Annalen, 1940, 543, 240—247).—Photoisopyrocalfiferol (I) is oxidised (CrO_3 , AcOH, 0°—room temp.) to photoisopyrocalfiferone, m.p. 79—



80°, $[\alpha]_D^{25} -116^\circ$ in CHCl_3 [*semicarbazone*, m.p. $\sim 210^\circ$ (decomp.)], which, like *photopyrocalfiferone*, m.p. 91° , $[\alpha]_D^{25} +197^\circ$ in CHCl_3 (*semicarbazone*, decomp. $\sim 210^\circ$), does not show absorption characteristic of an $\alpha\beta$ -unsaturated ketone. Photopyrocalfiferol (II) and (I) cannot, therefore, contain a 4:5 double linking. Ergosteryl acetate, photoisopyrocalfiferyl acetate (III), and the isobutyrate of (II) consume 3, 2, and 2 atoms of O, respectively, when titrated with BzO_2H in CHCl_3 . Reduction (H_2 , Pd-black, EtOAc) of (III) affords a H_4 -derivative, an oil; hydrolysis followed by oxidation gives the corresponding ketone (*semicarbazone*, m.p. 197°). A tetrahydrophotocalciferol can be similarly obtained. These results indicate that (I) and (II) contain 2 double linkings (1 in side-chain, 1 in ring B). During the formation of (I) and (II) from pyrocalfiferol, the second nuclear double linking is probably converted into a bridge (e.g., between $\text{C}_{(5)}$ and $\text{C}_{(8)}$ or $\text{C}_{(9)}$) (cf. A., 1937, II, 376).

H. B.

Steroids and sex hormones. LXII. $\Delta^5:17$ -3-*trans*-Hydroxy-17 α -methyl-D-homoandrostadiene and its transformation products. L. RUZICKA and H. F. MELDAHL (Helv. Chim. Acta, 1940, 23, 513—518).—The conversion of Δ^5 -17-acetylenylandrosterone-3:17-diol diacetate into Δ^5 -3:17 α -diacetoxy-17 α -methyl-D-homoandrostene-17-one (I), m.p. 191 — 193° , by $\text{HgO} + \text{SnCl}_4$, SiCl_4 , or $\text{HgO} + \text{FeCl}_3$ in $\text{AcOH}-\text{Ac}_2\text{O}$ is described. K_2CO_3 in boiling aq. MeOH hydrolyses (I) to the $(\text{OH})_2$ -compound, m.p. 273 — 275° , converted by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in $\text{C}_5\text{H}_{11}\text{ONa}$ at 200° into $\Delta^5:17$ -3-*trans*-hydroxy-17 α -methyl-D-homoandrostadiene (II), m.p. 162 — 164° , the acetate, m.p. 121 — 122° , of which is reduced (H_2 , PtO_2 , AcOH) to 3-*trans*-acetoxy-17 α -methyl-D-homoandrostane, m.p. 128 — 129° , hydrolysed to the alcohol, m.p. 161 — 163° . (II) is oxidised by $\text{Al}(\text{OBu}^t)_3$ in boiling $\text{COMe}_2-\text{C}_6\text{H}_6$ to $\Delta^4:17$ -17 α -methyl-D-homoandrostadien-3-one, m.p. 156 — 158° , reduced (H_2 , PtO_2 , AcOH) to 17 α -methyl-D-homoandrostane-3-one, m.p. 181 — 182° , and thence to 17 α -methyl-D-homoandrostane, m.p. 107 — 109° , $[\alpha]_D^{25} 2^\circ \pm 2^\circ$ in dioxan. All m.p. are corr. (vac.).

H. W.

Sterols. XX. Homogeneity of bessisterol and properties of its double linkings. S. KUWADA and S. YOSIKI (J. Pharm. Soc. Japan, 1939, 59, 282—284; cf. A., 1939, II, 431).—Bessisterol (I) fused with *p*-NPh $\cdot\text{N}-\text{C}_6\text{H}_4\cdot\text{COCl}$ gives an ester, m.p. 237.5 — 239.5° . (I) affords a 3:5-dinitrobenzoate, two forms, m.p. 202.5 — 205.5° and 199.5 — 204.5° , hydrolysed by $\text{KOH}-\text{EtOH}$ to (I), m.p. 175° , $[\alpha]_D^{25} -13.5^\circ$ (acetate, m.p. 185° ; benzoate, m.p. 202°). Hydrogenation of (I) gives bessistaenol, m.p. 113 — 115.5° (3:5-dinitrobenzoate, m.p. 206 — 209° ; acetate, m.p. 115.5 — 117.5°). (I) is homogeneous. M.p. are corr.

A. T. P.

Sterols. XXI. Constitution of bessisterol. S. KUWADA and S. YOSIKI (J. Pharm. Soc. Japan, 1940, 60, 25—27).—Bessisterol (I) is oxidised by $\text{Al}(\text{OPh})_3$ without change in the double linking to bessistenone (II), m.p. 180 — 181° (*semicarbazone*, decomp. 279.5° ; *oxime*, decomp. 257°), the absorption spectrum of which in hexane has max. at 240 and 280 — $290 \text{ m}\mu$. Hydrogenation (PtO_2 in EtOAc)

of (II) gives bessistaenol (III), m.p. 113.5 — 115.5° . Reduction (Meerwein-Ponndorf) of (II) gives substances (IV), m.p. 209 — 211.5° , and (V), m.p. 175° , both of which are pptd. by digitonin from EtOH . (IV) is identical with the compound obtained by heating (I) with NaOEt in a sealed tube. (V) has the same composition, $\text{C}_{29}\text{H}_{48}\text{O} \cdot 0.5\text{H}_2\text{O}$, as (I) but differs somewhat from it in absorption spectrum and $[\alpha]$; its 3:5-dinitrobenzoate and acetate are identical with those of (I). (III) is oxidised by a modified Oppenauer method to bessistaenone (VI), m.p. 116.5 — 120.5° (*oxime*, m.p. 186° ; *semicarbazone*, decomp. 245.5°), which re-forms (III) when catalytically reduced. Its absorption curve has a max. at $280 \text{ m}\mu$. It appears that Me at $\text{C}_{(10)}$ and OH at $\text{C}_{(3)}$ in (I) have the same steric arrangement as in cholesterol. Spectroscopic evidence negatives the presence of $\alpha\beta$ -unsaturated CO in (II) and (VI) and appears to indicate the existence of a simple CO. If the readily reduced double linking in (I) is not in the neighbourhood of OH it must occupy a position quite different from that assumed previously in order to avoid conjugation. All m.p. are corr.

H. W.

Sterols. XIX. Sterol from Coix seeds. S. KUNADA and S. YOSIKI (J. Pharm. Soc. Japan, 1939, 59, 203—204).—Extraction of the seeds of *Coix lacryma-jobi*, L. (var. *Frumentacea*, Makino), with Et_2O removes a fatty oil which when hydrolysed gives a sterol fraction which cannot be purified by the customary methods. It is therefore converted into the 3:5-dinitrobenzoate, m.p. 215 — 216° (corr.), $[\alpha]_D^{25} -7.3^\circ$ in CHCl_3 , which is hydrolysed to a sterol (I), $\text{C}_{29}\text{H}_{50}\text{O}$, m.p. 138.5° (corr.), $[\alpha]_D^{25} -19.5^\circ$, the absorption spectrum of which shows max. at 280 and $287 \text{ m}\mu$. (I) gives an acetate, m.p. 125° (corr.), $[\alpha]_D^{25} -37.2^\circ$ in CHCl_3 , and a benzoate, m.p. 147 — 149° (corr.), $[\alpha]_D^{25} -14.7^\circ$ in CHCl_3 . (I) absorbs 2 H_2 (PtO_2 in EtOAc) but the H_2 -derivative, m.p. 140.5 — 142.5° , $[\alpha]_D^{25} +23.5^\circ$ [which very obstinately retains $0.25\text{H}_2\text{O}$; it does not give a colour with $\text{C}(\text{NO}_2)_4$ in CHCl_3 or with Ac_2O in conc. H_2SO_4], only could be isolated. Evidence is afforded in favour of the view that (I) is very closely related to β -sitosterol and possibly contains a small proportion of α -sitosterol.

H. W.

Sterols. XCVI. alloPregnadiols from tigogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 898—900).— *ψ -Tigogenin*, m.p. 193 — 196° (prep. from tigogenin by Ac_2O at 195 — 200° and subsequent hydrolysis), and CrO_3-AcOH at 25 — 28° give $\Delta^{16:17}$ -allopregnene-3:20-dione, m.p. 210 — 212° , reduced by $\text{Na}-\text{EtOH}$ to allopregnane-3(β):20(α)-diol and by H_2 - PtO_2 in AcOH at 3 atm. to allopregnane-3(β):20(β)-diol (I). *ψ -Tigogenin* acetate and CrO_3-AcOH at 28° give a product which is reduced (H_2 , PtO_2 , AcOH) and then hydrolysed or oxidised (followed by hydrolysis) to (I) or allopregnane-3(β)-ol-20-one, respectively. The β -configuration of the $\text{C}_{(3)}\cdot\text{OH}$ is thus confirmed. R. S. C.

Lateral metallation of phenyl methyl sulphide. H. GILMAN and F. J. WEBB (J. Amer. Chem. Soc., 1940, 62, 987—988).— PhSMe and LiBu^t in Et_2O give after interaction with CO_2 35.2—43.5% of $\text{SPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, but PhOMe gives 32.4% of

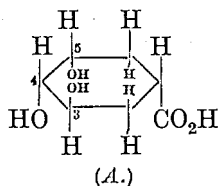
$o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and 5.37% of $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OMe-}o)_2$. PhSEt gives $o\text{-SEt}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. R. S. C.

Experiments on the synthesis of 1 : 2-dimethylcyclohexylacetic acid. F. C. CORP and J. L. SIMONSEN (J.C.S., 1940, 415—418; cf. A., 1939, II, 117).—2 : 3-Dimethylcyclohexanone (improved prep.) and $\text{NaNH}_2\cdot\text{C}_6\text{H}_6$ (in N_2), then $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, afford Et 6-keto-1 : 2- and Et 2-keto-3 : 4-dimethylcyclohexylacetate, b.p. 144°/16 mm., separated by condensing the former with $\text{Et}_2\text{C}_2\text{O}_4$ in EtOH-NaOEt at 0°; the resultant product, b.p. 160—180°/16 mm., and 10% aq. H_2SO_4 give keto-acids which afford an α -, m.p. 197—198°, and β -semicarbazone, decomp. 192° (softens at 187°), hydrolysed (dil. H_2SO_4) to α -6-keto-1 : 2-dimethylcyclohexylacetic acid, m.p. 107°, and a gum, respectively. 2-Methylcyclohexanone, $\text{NaNH}_2\cdot\text{Et}_2\text{O}$ (in N_2), and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ afford a product, b.p. 130—145°/16 mm., converted by $\text{Et}_2\text{C}_2\text{O}_4$ into Et 6-keto-5-carbethoxy-2-methylcyclohexylacetate, b.p. 170—190°/20 mm., which is hydrolysed by 10% aq. H_2SO_4 to 2-keto-1-methylcyclohexylacetic acid, m.p. 77—78° (semicarbazone, decomp. 182°). Its Et ester (I), b.p. 142°/19 mm., $\text{HCO}_2\text{C}_5\text{H}_{11}\text{-iso}$, and Na in Et_2O give the hydroxymethylene derivative (semicarbazone, m.p. 151°). (I) and MeMgI afford an oil, hydrolysed by $\text{KOH}\cdot\text{MeOH}$ to the lactone, m.p. 73°, of 6-hydroxy-1 : 2-dimethylcyclohexylacetic acid, which is converted by $\text{Zn}\cdot\text{Hg}$ in HCl into one of the theoretically possible forms of dl-1 : 2-dimethylcyclohexylacetic acid (II), b.p. 153°/16 mm.; its *p*-phenylphenacyl ester (III), m.p. 61—62°, on admixture with the *d*-ester (IV) from hydroxyeremophilone benzoate or with (V) (below) has m.p. 62—64°. (II) is resolved partly through the cinchonidine salt, m.p. 141—142°, $[\alpha]_{5461}^{20} - 95^\circ$ in CHCl_3 , into the *l*-acid [*p*-phenylphenacyl ester (V), m.p. 65—67°, $[\alpha]_{5461}^{20} - 6^\circ$ in EtOAc]; the latter mixed with (IV) in Et_2O affords a product, m.p. 62—63° [unchanged by (III)]. Acidification of the solution from the cinchonidine salt gives the *d*-acid [*p*-phenylphenacyl ester, m.p. 62—65°, $[\alpha]_{5461}^{20} + 8^\circ$ in EtOAc]. In eremophilone and hydroxyeremophilone, the Me groups occupy the 1 : 10-positions; the ketones are not isoprene derivatives. A. T. P.

Resolution of dl- Δ^2 -cyclogeranic acid. D. J. BENNETT, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1940, 418—419).—dl- Δ^2 -cyclogeranic acid is resolved by the half-mol. method. The cinchonine salt, m.p. 204—206° (sinters at 183°), $[\alpha]_{5461}^{20} - 15.4^\circ$ in CHCl_3 , gives the *l*-acid, m.p. 104°, $[\alpha]_{5461}^{20} - 395.7^\circ$ in EtOH; the acid, $[\alpha]_{5461}^{20} + 200^\circ$ in EtOH, from the more sol. salt is converted into the cinchonidine salt, m.p. 157—158°, $[\alpha]_{5461}^{20} + 81.1^\circ$ in CHCl_3 , and thence into the *d*-acid, m.p. 104°, $[\alpha]_{5461}^{20} + 395.7^\circ$ in EtOH. Neither acid is identical with the acid, $\text{C}_{10}\text{H}_{16}\text{O}_2$, m.p. 83° (cf. A., 1939, II, 514). A. T. P.

Steric series. XXIII. Configuration of the tertiary carbon atom. III. K. FREUDENBERG, H. MEISENHEIMER, J. T. LANE, and E. PLANKENHORN (Annalen, 1940, 543, 162—171; cf. A., 1933, 502; 1934, 757).—In order to determine the mesoid or racemoid character of a compound, $\text{OH}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{X}$, containing 2 asymmetric centres (configuration of

* known, that of † unknown), it is necessary that R. and R' should be joined in a ring and that the *cis* or *trans* relationship of OH and X be known. Subsequent destruction of centre * (e.g., $\text{CH}\cdot\text{OH} \rightarrow$



CH_2) allows the configuration of centre † to be determined. These principles are applied to dihydroshikimic acid (A) (configuration of $\text{C}_{(3)}$ as in glucodesonic acid) (cf. Fischer *et al.*, A., 1937, II, 382), which is cleaved between $\text{C}_{(4)}$ and $\text{C}_{(5)}$ (after protection of $\text{C}_{(3)}\cdot\text{OH}$ as

$\text{C}_{(3)}\cdot\text{OMe}$), leading to

$\text{CO}_2\text{Me}\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ (B). This is converted by fuming HI at 180° into (probably) non-homogeneous *d*(+)- β -carboxyadipic acid, m.p. ~116°, $[\alpha]_{\text{D}}^{20} + 12.6^\circ$ (max.) in COMe_2 (crystallisation from EtOAc gives some *dl*-acid, m.p. 122—123°). 4 : 5-isoPropylideneshikimic acid (I), MeI, and Ag_2O in COMe_2 afford *Me* 3-methyl-4 : 5-isopropylideneshikimate, b.p. 108—112°/0.4 mm., $[\alpha]_{\text{D}}^{20} - 51.5^\circ$ in EtOH, hydrolysed [30% AcOH at 100° (bath) followed by aq. $\text{Ba}(\text{OH})_2$ at 50°] to 3-methylshikimic acid, m.p. 122—123°, $[\alpha]_{\text{D}}^{20} - 190^\circ$ in H_2O , which is reduced (H_2 , Pd, H_2O) to 3-methyldihydroshikimic acid (II), m.p. 124.5°, $[\alpha]_{\text{D}}^{20} - 22^\circ$ in H_2O (*Me* ester, $[\alpha]_{\text{D}}^{20} - 12^\circ$ in EtOH). HI (*d* 1.7) at 50—55° converts (II) into (A), whilst oxidation [$\text{Pb}(\text{OAc})_4\text{-AcOH}$ followed by aq. $\text{K}_2\text{CO}_3\text{-KMnO}_4$] gives β -carboxy- δ -methoxyadipic acid [*Me*₃ ester (= B), b.p. 116° (bath)/0.1 mm., $[\alpha]_{\text{D}}^{20} + 51.2^\circ$ in COMe_2 ; triamide, m.p. 186°, $[\alpha]_{\text{D}}^{20} + 33.5^\circ$ in H_2O]. Fission of (II) with $\text{Pb}(\text{OAc})_4$, conversion of the resultant dialdehyde into the di-oxime, and dehydration to the dinitrile also affords, less well, a route to (B). Hydrolysis [aq. $\text{Ba}(\text{OH})_2$] of Et $\alpha\beta$ -dicyanobutane- δ -carboxylate (Leuchs *et al.*, A., 1909, i, 361) affords *dl*- β -carboxyadipic acid, resolved by brucine into the *l*-, m.p. 105—107°, $[\alpha]_{\text{D}}^{20} - 15.5^\circ$, and *d*-acid, $[\alpha]_{\text{D}}^{20} + 15.5^\circ$ in COMe_2 (cf. above). H. B.

A little known reaction for benzoic acid. N. SCHOORL (Pharm. Weekblad, 1940, 77, 425—427; cf. Guerbet, A., 1920, ii, 517).—The sample is evaporated to dryness with HNO_3 (*d* 1.50), the residue dissolved in NaOH and reduced with 10% SnCl_2 and 4*N*-HCl. Sn is pptd. from the cold acid solution with Al, NaNO_2 is added, and the diazotised *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ coupled with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ in aq. NH_3 . The red azo-dye is also obtained from cinnamic acid; *o*- and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ interfere. The reaction is sensitive to 0.1 mg. of BzOH. S. C.

Reactivity of atoms and groups in organic compounds. XX. Effect of substituents on the relative reactivities of the hydroxyl group in derivatives of benzoic acid. J. F. NORRIS and A. E. BEARSE (J. Amer. Chem. Soc., 1940, 62, 953—956; cf. A., 1939, II, 369).—The rate of formation of chlorides from BzOH and its derivatives with SOCl_2 shows that reactivity of the OH is inversely related to the reactivity of the acidic H. Thus the increasing activation by substitution is 2 : 6-(OMe)₂ > *p*-OMe > 2 : 4 : 6-Me₃ > 2 : 4 : 6-Et₃ > *o*-OMe > *p*- > *m*- > *o*-Me > H > *o*- > *m*-Cl > 2 : 6-Cl₂ > 2-chloro-6-nitro > *o*- > *m*-NO₂. *NN*-Dimethylcyclohexylamine and

C_5H_5N catalyse the reaction, particularly with *o*-substituted derivatives. R. S. C.

Alkanolamines. VIII. Reaction of ethanolamines with *p*-nitrobenzoic acid. M. MELTSNER, D. GREENFIELD, and H. ROSENZWEIG (J. Amer. Chem. Soc., 1940, 62, 991–992).—Mono- (I), di- (II), or tri-ethanolamine (1 mol.) with $p\text{-NO}_2\cdot C_6H_4\cdot CO_2H$ (III) (1 mol.) at 100° gives the salts, m.p. 168°, 138°, and 116°, respectively. 1 mol. each of (I) and (III) under reflux give some $p\text{-NH}_2\cdot C_6H_4\cdot CO_2H$ (IV) and *di*(ethanolamine) *p*-azoxybenzoate, m.p. 130°. (II) (4 mols.) and (III) (1 mol.) at 180° give (IV). R. S. C.

Ferrisalicylic complexes. G. ILLARI (Annali Chim. Appl., 1940, 30, 65–72).—Salicylic acid with $FeCl_3$ gives a violet-coloured complex, $C_6H_4(O\cdot FeCl_2)\cdot CO_2H$, and, in presence of $NaHCO_3$, a violet-coloured complex $C_6H_4[O\cdot Fe(OH)_2]\cdot CO_2H$; the structures of these complexes are discussed (cf. A., 1931, 1022). In presence of 0.01N-HCl, a more intensely coloured complex, $C_6H_4(O\cdot FeCl_2)\cdot CO_2FeCl_2$, is formed. F. O. H.

4 : 5-Dimethylacetylsalicylic acid. L. BIRKOFER (Z. physiol. Chem., 1939, 261, 87–92).—1 : 2 : 4- $C_6H_3Me_2\cdot ONa$ and CO_2 at 170°/35 atm. give 4 : 5-dimethylsalicylic acid, m.p. 200° [*Ac* derivative (I), m.p. 122° or 112°; *Na* salt; *Me*, m.p. 33° (*Ac* derivative, m.p. 74–75°), and *Ph* ester, m.p. 85°]. (I) is extremely analgesic (rabbits, monkeys, humans), as bactericidal as aspirin, and less toxic orally (rabbits) and no more toxic intravenously (mice). R. S. C.

Chloralamides. Reaction of phosphorus pentachloride on choral-chlorosalicylamides and their methyl ethers, and the reactivity of the chlorine atom. N. W. HIRWE and K. N. RANA (J. Indian Chem. Soc., 1939, 16, 677–680).—2 : 5 : 1- $OMe\cdot C_6H_3Cl\cdot CO\cdot NH\cdot CH(OH)\cdot CCl_3$ (I) and PCl_5 give α -chlorochloral-5-chloro-2-methoxybenzamide, m.p. 144–145°, which with H_2O regenerates (I) and with the appropriate reagent gives α -methoxy-, α -ethoxy-, m.p. 137–138°, α -anilino-, m.p. 152–153°, *o*-, m.p. 148–149°, *m*-, m.p. 153–154°, and *p*-toluidino-, m.p. 169–170°, α -phenoxy-, m.p. 194–195°, and α -benzoyloxy-chloral-5-chloro-2-methoxybenzamide, m.p. 133–135°. α -Chloro-, m.p. 89–91°, α -methoxy-, α -anilino-, m.p. 147–148°, α -phenoxy-, m.p. 125–126°, *o*-, m.p. 153–154°, *m*-, m.p. 146–147°, and *p*-toluidino-chloral-3 : 5-dichloro-2-methoxybenzamide, m.p. 145–146°, are similarly prepared. F. R. S.

Metalation of alcohols and amines. H. GILMAN, G. E. BROWN, F. J. WEBB, and S. M. SPATZ (J. Amer. Chem. Soc., 1940, 62, 977–979).— $CH_2Ph\cdot OH$ and $LiBu^a$ (~2 mols.) in Et_2O give after reaction with CO_2 8.7% of phthalide + $o\text{-CO}_2H\cdot C_6H_4\cdot CH_2\cdot OH$. $CH_2Ph\cdot OMe$ gives similarly $o\text{-CO}_2H\cdot C_6H_4\cdot CH_2\cdot OMe$. $CHPh_2\cdot OH$ gives 18.6% of α -phenylphthalide. $CPh_3\cdot OH$, best in presence of Cu-bronze, gives 4.85% of the lactone of triphenylcarbinol-2 : 2'-dicarboxylic acid. NH_2Ph gives 4.2% of $o\text{-NH}_2\cdot C_6H_4\cdot CO_2H$ (I). $NHPh_2$ gives 10.9–14.7% of $o\text{-NHPh}\cdot C_6H_4\cdot CO_2H$. $NHPhBu^a$ gives 2% of *N*-*n*-butylanthranilic acid, m.p. 80–81°, also obtained from (I) by $Bu^aBr\cdot K_2CO_3$. NPh_3 gives (Cu-bronze) mixed acids. Piperidine gives an oil. R. S. C.

Synthesis of growth-inhibitory polycyclic compounds. II. G. M. BADGER and J. W. COOK (J.C.S., 1940, 409–412; cf. A., 1939, II, 315).—1 : 2-Benzanthracene and $Br\cdot CS_2$ yield the 10-*Br*- (I), m.p. 147.5–148.5° (*picrate*, m.p. 155.5–156.5°), converted by $Cu_2(CN)_2$ in $CH_2Ph\cdot CN$ at 190–200° followed by hot aq. HCl, into the 10-CN-derivative, m.p. 187.5–188.5° (corr.) (cf. Fieser *et al.*, A., 1938, II, 493); the latter does not react with MeMgI and is not reduced by $H_2\cdot Pt$ or Zn-Hg in HCl-AcOH. It is hydrolysed by KOH-MeOH, but not by $H_2SO_4\cdot AcOH$, to 1 : 2-benz-10-anthramide, m.p. 218–220°, Mg 1 : 2-benz-10-anthranyl bromide [from (I), EtBr, and Mg in $Et_2O\cdot C_6H_6$] and $(CH_2)_2O$ give 10- β -hydroxyethyl-1 : 2-benzanthracene, m.p. 181.5–182.5°. 1 : 2-Benz-10-anthraldehyde (II) and ice-cold $KMnO_4\cdot COMe_2$ yield 1 : 2-benz-10-anthroic acid (cf. Dansi, A., 1937, II, 285). 1 : 2-Benzanthracene, $COCl\cdot CO_2Et$, and $AlCl_3$ in $PhNO_2$ at 0°, then at room temp., give 1 : 2-benzanthranyl-10-glyoxylic acid, m.p. 175–176.5° (decomp.), reduced by Na-Hg in dil. NaOH to α -hydroxy-1 : 2-benzanthranyl-10-acetic acid, m.p. 187–191°, or by red P and HI (*d* 1.7) in AcOH to 1 : 2-benzanthranyl-10-acetic acid (III), m.p. 270–274° (previous sintering). 10-Chloromethyl-1 : 2-benzanthracene and KCN-aq. $COMe_2$ or $Cu_2(CN)_2$ in $CH_2Ph\cdot CN$ at 180–190° followed by C_6H_6 -conc. HCl afford 10-cyanomethyl-1 : 2-benzanthracene, m.p. 177–178°, hydrolysed by 15% KOH-EtOH to (III). (II) and CH_2N_2 in MeOH- Et_2O give (?) 1 : 2-benzanthranyl-10-acetaldehyde, m.p. 146–147° [$s\text{-C}_6H_3(NO_2)_3$ complex, m.p. 149–150°; *picrate*, m.p. 138.5–139.5°], oxidised by $Na_2Cr_2O_7\cdot AcOH$ to 1 : 2-benzanthraquinone. 9-Methyl-1 : 2-benzanthracene (IV) and $Br\cdot CS_2$ afford a 10-*Br*-derivative, m.p. 122–123°, converted by $Cu_2(CN)_2$ in $CH_2Ph\cdot CN$ at 190–200° into 10-cyano-9-methyl-1 : 2-benzanthracene, m.p. 151.5–152°. $HCO\cdot NPhMe$, (IV), and $POCl_3$ in $o\text{-C}_6H_4Cl_2$ at 100° (bath) yield 9-methyl-1 : 2-benz-10-anthraldehyde, m.p. 111.5–112.5°. 6-Methyl-1 : 2-benzanthracene (V) and $Br\cdot CS_2$ afford the 10-*Br*-derivative, m.p. 138–139° (oxidised by $Na_2Cr_2O_7\cdot AcOH$ to 6-methyl-1 : 2-benzanthraquinone), converted into 10-cyano-6-methyl-1 : 2-benzanthracene, m.p. 203.5–204.5°. (V) and paraformaldehyde in HCl-AcOH at 60° give a CH_2Cl compound, converted by KOAc-AcOH into 6-methyl-10-acetoxymethyl-1 : 2-benzanthracene, m.p. 168.5–169.5°, and thence by aq. EtOH-NaOH into the 10- $OH\cdot CH_2$ compound, decomp. 220–230° (previous sintering). Tests [by A. HADDOW] show that of the 10-substituted benzanthracenes examined, only 1 : 2-benz-10-anthraldehyde and Na 1 : 2-benz-10-anthroate (H_2O -sol.) produce a characteristic inhibition of growth, of moderate intensity; a definite effect is also noted with 10-cyano- and 10-cyano-6-methyl-1 : 2-benzanthracene. Introduction of OH and CO_2H groups is attended by marked loss of growth-inhibitory activity. Tests for carcinogenic activity are recorded. A. T. P.

Optical study and synthesis of unsymmetrical phthaleins and their derivatives. L. C. KIN (Ann. Chim., 1940, [xi], 13, 317–399).—Attempts to obtain methoxylated *o*-benzoylbenzoic acids by use of $AlCl_3$ under the customary conditions generally

give poor yields of impure products owing to elimination of Me but good results are secured by the use of PhNO_2 as solvent at $<5^\circ$. Thus are obtained $o\text{-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$ (Me ester has m.p. 52°); $2\text{-}p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (I), m.p. 145° , of which only one Me ester, m.p. 82° , could be isolated; $o\text{-}4'\text{-hydroxy}$, m.p. $187\text{--}188^\circ$, and $o\text{-}4'\text{-methoxy-}2'\text{-methyl-}5'\text{-isopropylbenzoylbenzoic acid}$, m.p. $155\text{--}156^\circ$; $o\text{-}2\text{-}4$, m.p. 164° , and $o\text{-}3\text{-}4\text{-dimethoxybenzoylbenzoic acid}$, m.p. 234° . By condensation of the requisite acid chloride with the necessary phenol or phenolic ether the following are obtained: $\alpha\text{-phenyl-}\alpha\text{-}p\text{-anisylphthalide}$, m.p. 115° , also obtained with $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Bz}$, m.p. 134° (diazine, m.p. 161°), from (I) and MgPhBr ; $\alpha\text{-phenyl-}\alpha\text{-}p\text{-hydroxyphenylphthalide}$, m.p. 171° ; lactonic Me, m.p. 128° , and Me_2 , m.p. 103° , ether of phenolphthalein; lactonic Me_2 ether, m.p. 122° , of phenolthymolphthalein; $\alpha\text{-}p\text{-hydroxyphenyl-}\alpha\text{-}4'\text{-methoxy-}2'\text{-methyl-}5'\text{-isopropylphenylphthalide}$, m.p. $195\text{--}200^\circ$ after softening at 160° ; lactonic Me_2 ether, m.p. 177° , of thymolphthalein; phenolresorcinolphthalein Me_3 ether, m.p. 230° ; phenolpyrocatecholphthalein Me_3 ether, m.p. 98° ; phenolquinolphthalein Me_3 ether, m.p. 176° ; thymolpyrocatecholphthalein Me_3 ether, m.p. 158° ; thymolresorcinolphthalein Me_3 ether, m.p. 168° ; phenylpyrocatechol, new m.p. $170\text{--}171^\circ$, phenylquinol, m.p. 248° , methylthymolpyrocatechol, m.p. 230° , methylthymolresorcinol, m.p. $210\text{--}211^\circ$, phenolthymol, m.p. 276° , phenolresorcinol, m.p. 205° , phenolpyrocatechol (triacetate, m.p. 148°), phenolquinol, m.p. $240\text{--}245^\circ$ (decomp.) after softening at 220° , thymolpyrocatechol, m.p. 284° , and thymolresorcinol, m.p. $284\text{--}285^\circ$, -phthalein. Reduction of the requisite phthalein with Zn dust and NaOH leads to the following -phthalins: phenylpyrocatechol, m.p. 159° ; phenolthymol, m.p. 209° ; phenolresorcinol, m.p. $288\text{--}290^\circ$. $1\text{:}4\text{-Di-}p\text{-hydroxybenzoylbenzene}$ has m.p. 225° . Spectroscopic evidence proves that $o\text{-arylbenzoic acids}$ in solution are ketones and not OH-lactones. Phenolphthalein is not diketonic but quinonoid in alkaline solution. The intense coloration of the phthaleins is developed only if they contain at least two phenolic OH which may be present in the same aromatic nucleus. All the phthaleins contain the no. of active H required by their customary formulæ and Oddo's modifications are unnecessary. The stability of the different possible forms of the phthaleins varies with solvent, temp., p_H , and the structure of the rest of the mol. The presence of two phenolic OH attached to the same aromatic nucleus causes a more or less ready scission of the mol. in alkaline solution and the dihydric phenol is invariably liberated. The introduction of phenolic OH into the mol. of a phthalein has a profound influence on the colour in alkaline solution, and the position of OH relative to the other chromophores is also important. When the quinonoid grouping can be developed in two nuclei of a phthalein mol., a mixture of isomerides always appears to result.

H. W.

Addition compounds of phthaleins and metallic salts. G. SACHS and L. RYFFEL-NEUMANN (J. Amer. Chem. Soc., 1940, 62, 993–994).—The follow-

ing additive compounds are prepared: phenolphthalein, SnCl_4 , + PhNO_2 , m.p. $78\text{--}79^\circ$, + PhOMe , or + PhCN ; phenolphthalein Me_2 ether (A) gives A, SnCl_4 , m.p. 128° , 2A, SnCl_4 , and A, SbCl_5 ; 3:6-dimethylfluoran (X) gives X, SnCl_4 , X, SnCl_4 , PhOMe , 2X, 3 SnCl_4 , 2 PhOMe , m.p. 139° (decomp.), X, SbCl_5 , m.p. 203° , and X, SbCl_5 , HCl , AcOH , m.p. 203° ; 2fluorescein, SnCl_4 ; fluorescein Me_2 ether, SnCl_4 .

R. S. C.

Preparation of aurintricarboxylic acid. D. A. HOLADAY (J. Amer. Chem. Soc., 1940, 62, 989).—Prep. of the acid (97% pure) from $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}]_2$, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $\text{NaNO}_2\text{-H}_2\text{SO}_4$ is improved.

R. S. C.

Total synthesis of a non-benzenoid steroid. L. W. BUTZ, A. M. GADDIS, E. W. J. BUTZ, and R. E. DAVIS (J. Amer. Chem. Soc., 1940, 62, 995–996).— $\alpha\text{-}\Delta^1\text{-cyclo-Hexenyl-}\beta\text{-}\Delta^1\text{-cyclopentenyl-acetylene}$ and $(\text{CH}_3\text{CO})_2\text{O}$ (1 mol.) at 130° give $\Delta^{8(14):9}\text{-steradiene-}6\text{:}7\text{:}11\text{:}12\text{-tetracarboxylic dianhydride}$ (I), m.p. $249\text{--}251^\circ$ (corr.; decomp.), converted by Pd-C in low yield into $1\text{:}2\text{-cyclopentenophenanthrene}$, m.p. $132\text{--}133^\circ$ (corr.).

R. S. C.

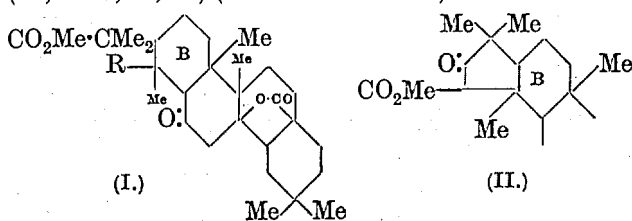
Bile acids. LVII. M. SCHENCK (Z. physiol. Chem., 1939, 261, 273–277).—The keto-oximino-hydroxamic acid, $\text{C}_{24}\text{H}_{36}\text{O}_8\text{N}_2$ (cf. A., 1935, 213), and KMnO_4 give cilianic (? by way of bilianic) acid and ~ 0.3 equiv. of $(\text{N}_2 + \text{N}_2\text{O})$.

R. S. C.

Saponins and sterols. XV. Dry distillation of ursolic acid with selenium, and its constitution. K. FUJII and S. OOSUMI (J. Pharm. Soc. Japan, 1939, 59, 264–268).—Ursolic acid (I) with Se at $330\text{--}350^\circ/36$ hr. gives sapotalene, $1\text{:}2\text{:}3\text{:}4\text{-C}_6\text{H}_2\text{Me}_4$, $2\text{:}7\text{-C}_{10}\text{H}_6\text{Me}_2$, $1\text{:}2\text{:}5\text{:}6\text{-C}_{10}\text{H}_4\text{Me}_4$, and $1\text{:}5\text{:}6\text{:}2\text{-C}_{10}\text{H}_4\text{Me}_3\text{OH}$ (cf. Drake et al., A., 1936, 1386; Ruzicka et al., A., 1937, II, 202). The appended structure for (I) (R or R' = CO_2H or Me) indicates a skeleton structure similar to that of oleanolic acid. (I) and $\text{ZnCl}_2\text{-AcOH}$ give ursylenic acid, m.p. 265° (corr.).

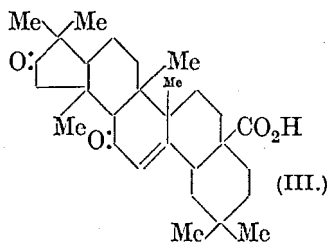
A. T. P.

Saponins. XV. Constitution of nitro-compounds of the oleanolic acid series. I. S. KUWADA and K. TAKEDA (J. Pharm. Soc. Japan, 1939, 59, 294–298).— Me_3 nitro-oleanoltricarboxylate (A., 1940, II, 89) (structure modified) with Zn-AcOH



at 100° yields the Me_2 ester lactone [(I)]; $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Me}$, m.p. $229\text{--}232^\circ$, $[\alpha]_D^{25} + 98.5^\circ$, which

with boiling 10% MeOH-KOH gives a mixture of a *diketolactone* Me ester (II), decomp. 315–318°, $[\alpha]_D^{25}$ –37.7° (monoxime, decomp. 266–266.5°), and a *diketo-monocarboxylic acid* (III), decomp. 359–361°, $[\alpha]_D^{25}$ +73.4°. The nitro-ketonic ester (*loc. cit.*) (structure modified) is converted by Zn-AcOH into a *diketo-lactone* [as (II), CO₂Me = H], decomp. 306–308°, $[\alpha]_D^{25}$ +209.5° (monoxime, decomp. 298–300°), which with KOH-MeOH affords (III). Me₃ nitro-oleanintricarboxylate (*loc. cit.*) with boiling Zn-AcOH yields the Me₂ ester lactone, [(I); R = CO₂Me], m.p. 237–240°, $[\alpha]_D^{25}$ +97.7°. M.p. etc. are corr.



J. D. R.

Aldehydic perfumes. IV. Synthesis of α -vanillylidene- and α -salicylidene-*n*-heptaldehyde. S. ISHIKAWA and T. SAKURAI (Sci. Rep. Tokyo Bunrika Daigaku, 1939, 3, 291–292).—Vanillin or *o*-OH-C₆H₄-CHO with *n*-C₆H₁₃-CHO and NaOH in ~50% EtOH give α -vanillylidene- (21%), b.p. 119°/2 mm. [2:4-dinitrophenylhydrazones, m.p. 130.5° (corr.; block)], or α -salicylidene-*n*-heptaldehyde (36.7%), b.p. 124°/3.5 mm. [2:4-dinitrophenylhydrazones, m.p. 128.6° (corr.; block)], respectively.

R. S. C.

Thermal decomposition of gaseous benzaldehyde.—See A., 1940, I, 259.

Nitration of 1-naphthaldehyde. P. RUGGLI and E. BURCKHARDT (Helv. Chim. Acta, 1940, 23, 441–445).—1-C₁₀H₇-CHO is converted by HNO₃ (*d* 1.52) at –15° mainly into (NO₂)₂-derivatives but by HNO₃ (*d* 1.47) at –5° to 0° into a mixture not separable from one another by crystallisation. It is therefore converted into the separable *anils*, m.p. 114–115° and 83–84°, of 8-nitro-1-naphthaldehyde, m.p. 123–124°, and 5:1-NO₂-C₁₀H₆-CHO, m.p. 136–137°, respectively, which are oxidised to 8:1- and 5:1-NO₂-C₁₀H₆-CO₂H, m.p. 236–237°, respectively.

H. W.

Nitration of 2-naphthol-1-aldehyde. P. RUGGLI and E. BURCKHARDT (Helv. Chim. Acta, 1940, 23, 445–449).—2:1-OH-C₁₀H₆-CHO, m.p. 84° (prep. from β -C₁₀H₇-OH and HCO-NH₂ described), is converted by HNO₃ (*d* 1.47) at –5° to 0° into 6-nitro-2-naphthol-1-aldehyde, m.p. 239°, transformed by Me₂SO₄-KOH-MeOH into the *Me ether* (I), m.p. 174°, preferably obtained by nitration of 2:1-OMe-C₁₀H₆-CHO. (I) is oxidised (KMnO₄-KOH) to 6-nitro-2-methoxy-1-naphthoic acid, m.p. 187–188°, decarboxylated (Cu powder in quinoline at 170°) to 6:2-NO₂-C₁₀H₆-OMe.

H. W.

Disubstituted aminoacetones containing two dissimilar substituents. J. W. MAGEE [with H. R. HENZE] (J. Amer. Chem. Soc., 1940, 62, 910–912).—COMe-CH₂-Br (1 mol.) with NHRR' (2 mols.) in Et₂O or NHRR' (1 mol.) and aq. Na₂CO₃ gives (figures in parentheses are m.p. of the *semicarbazones*) *N*-methyl-, b.p. 110.7°/3 mm. (158°), -ethyl-, b.p. 123.5°/3 mm. (140°), and -benzyl-anilinoacetone, b.p. 187.9°/4.5 mm. (141°), *N*-methyl-, b.p. 129.5°/16 mm.

(132°), -ethyl-, b.p. 113.8°/3 mm. (135°), -*n*-propyl-, b.p. 130°/6 mm. (125°), and -*n*-butyl-benzylaminoacetone, b.p. 147.5°/8 mm. (113°), *N*-o-, b.p. 137.3°/10 mm. (134°), and -*p*-methylbenzylmethylaminoacetone, b.p. 132.3°/9 mm. (133°), and -cyclohexylmethylaminoacetone, b.p. 93.2°/4 mm. (171°). *N*-cyclohexylmethylamine is prepared by hydrogenating (Raney Ni) NHPMe at 200°/233 atm. NHR-CH₂-Ar are prepared by heating ArCHO and NH₂R at 100°, removing the H₂O formed, and hydrogenating the residue at 75°/133 atm. Temp. are corr. *n*, *d*, and parachors are recorded.

R. S. C.

Condensation of methylzingerone. T. KOBAYASHI and T. IWASAKI (Sci. Rep. Tôhoku, 1940, 28, 297–303).—Methylzingerone (β :3:4-dimethoxyphenylethyl Me ketone) (cf. Nomura, A., 1917, i, 570) and HCl in AcOH or EtOH at room temp./5 days give 1:3:5-tri-(β :3':4'-dimethoxyphenylethyl)benzene, m.p. 144–145°, oxidised by aq. KMnO₄ at 100° (bath) to 1:3:5-C₆H₃(CO₂H)₃ and 3:4:1-(OMe)₂C₆H₃-CO₂H.

A. T. P.

Hexahydroacetomesitylene. E. P. KOHLER, T. L. JACOBS, and H. M. SONNICHSEN (J. Amer. Chem. Soc., 1940, 62, 785–793).—The CO of hexahydroacetomesitylene is slightly less hindered than that of acetomesitylene. Hydrogenation [Raney Ni, activated by (NH₄)₂PtCl₆; 250°/240 atm.; H₂O] of Na mesitylenecarboxylic gives mixed hexahydroacetomesitylenecarboxylic (2:4:6-trimethylcyclohexane-1-carboxylic) acids, yielding an *amide* (I), m.p. 230°, and a mixed *amide* (II), m.p. 167°, containing (I). NaNO₂-AcOH and (I) give an *acid*, m.p. 86–87°; (II) gives a small amount of an *acid* (? impure), m.p. 114–117° (sinters at 100°). MgMeCl converts (I) into 2:4:6-trimethylhexahydrobenzonitrile, b.p. 66–71°/3 mm. 2:4:6-Trimethylcyclohexane-1-carboxyl chloride (III) (prep. by SOCl₂) and boiling MeOH give the *Me* ester, b.p. 90–96°/14 mm., which with MgMeCl gives a small amount of 1:3:5-trimethyl-2-isopropenylcyclohexane (IV), b.p. 70.8–71.2°/10 mm. MgMeCl and (III) in Et₂O-C₆H₆ give hexahydroacetomesitylene (V) (70%), b.p. 86–87°/9 mm. (obtained also in 55% yield by ZnMeCl), hexahydroacetomesityldimethylcarbinol (VI) (16%), m.p. 67–69°, b.p. 106°/10 mm., and (IV) (5.5%). (V) reacts only slowly with MgRHal. MgMeI and (VI) give 1.12 mols. of CH₄. PhNCO dehydrates (VI), yielding CO(NHPH)₂; AcCl, Ac₂O, or NaOBr gives (IV). With HCl-EtOH, (VI) gives an unstable chloride, b.p. 94.6–97.1°/9 mm. O₃ yields CH₂O from (IV), but no (V) could be isolated. Br and (IV) in CCl₄ afford a product, which soon gives HBr and *inter alia* 1:3:5-trimethyl-2- β -bromo- α -methylvinylcyclohexane, m.p. 41–42°. 2:4:6:1-C₆H₂Me₃-COCl and MgMeCl give 90% of acetomesitylene and >1–2% of the alcohol. Na-CMe₂-Et-OH reduces (V) to hexahydroacetomesityldimethylcarbinol, b.p. 94–99.5°/8 mm. (phenylurethane, m.p. 132–134°). NaOBr and (V) give slowly dibromoacetohexahydroacetomesitylene, m.p. 63–65°, and only a trace of acid. Condensation of (V) with aldehydes is difficult, but by use of NaNH₂-C₆H₆ the *CHPh* derivative (VII), m.p. <0°, b.p. 148°/0.5 mm., is obtained; this gives a *dibromide*, m.p. 211–212° (slight decomp.), which with hot KOH-MeOH gives

90% of $\alpha\gamma$ -diketo- γ -hexahydromesityl- α -phenylpropane, m.p. 197—199°. Hydrogenation (PtO₂) of (VII) gives β -phenylpropiohexahydromesitylene, b.p. 180—182°/8 mm. MgPhBr converts (VII) into $\beta\beta$ -diphenylpropiohexahydromesitylene, m.p. 78—80°, which gives *enol peroxides*, m.p. 86—87° (VIII) (main product) and 119—121°. Hydrogenation (PtO₂) of (VIII) gives a *substance*, C₂₄H₃₀O₂, m.p. 86—87°, and thermal decomp. gives mainly a *hydrocarbon*, m.p. 200—205°.

R. S. C.

Carbon suboxide in the Friedel-Crafts reaction.

I. J. H. BILLMAN, G. E. TRIPP, and R. V. CASH (J. Amer. Chem. Soc., 1940, 62, 770—771).—C₃O₂ (previously described), C₆H₆, and AlCl₃ at $\sim 4^\circ$ and then at the b.p. give a little CPhMe (formed by way of CPh·CH₂·CO₂H) and much polymeric C₃O₂.

R. S. C.

Chloromethylation of aryl ketones. R. C. FUSON and C. H. MCKEEVER (J. Amer. Chem. Soc., 1940, 62, 784—785).—The appropriate ketone, para-formaldehyde, and conc. HCl at 25—85° give 2:4-dimethyl-5-, m.p. 68.5—69°, and 2:4:6-triethyl-3-chloromethylacetophenone, m.p. 57—58°, 3-chloromethyl-aceto-, m.p. 74.5—75.5°, -propio-, m.p. 75—76°, -isobutyro-, b.p. 140°/2 mm., -pivalyl-, m.p. 54—55°, and -benzoyl-, m.p. 90—91°, -mesitylene, and 3-chloromethylacetoisodurene, m.p. 88.5—90°. Pivalylmesitylene has b.p. 97—97.5°/2.5 mm.

R. S. C.

C-Alkylresorcinols. IV. **Nuclear methylation of 4-acylresorcinols.** H. A. SHAH and R. C. SHAH (J. Indian Chem. Soc., 1940, 17, 32—36; cf. A., 1939, II, 373).—Resorpiophenone, MeI, and MeOH-KOH afford 2-hydroxy-4-methoxy-3-methylpropiofenone (I), m.p. 78—79°, demethylated by AlCl₃ at 135—140° or Ac₂O-HI (*d* 1.7) at 130—140° to 2:4-dihydroxy-3-methylpropiofenone, m.p. 128—130°, also obtained from 2:1:3-C₆H₃Me(OH)₂ (II) and EtCN (Hoesch). (I) and Ac₂O-NaOAc at 175—185° afford 7-methoxy-2:3:8-trimethylchromone (+H₂O), m.p. 69—70°, hydrolysed by boiling 5% aq. NaOH to (I) and 2:3:4:1-OH·C₆H₂Me(OMe)·CO₂H. Resbutyrophenone similarly gives 2-hydroxy-4-methoxy-3-methylbutyrophenone (III), m.p. 82—84°, and thence the 2:4-(OH)₂-compound, m.p. 155—157° [also from (II) and PrCN], and 7-methoxy-2:8-dimethyl-3-ethylchromone, m.p. 43—45°, hydrolysed to (III) and 2:4:3:1-(OMe)₂C₆H₂Me·CO₂H. 2:4-Dihydroxyphenyl benzyl ketone affords 2-hydroxy-4-methoxy-3-methylphenyl benzyl ketone, m.p. 110—111°, and thence the 2:4-(OH)₂-compound, m.p. 157—159° [also from (II) and CH₂Ph·CN], and 7-methoxy-2:8-dimethylisoflavone, m.p. 140—142°. 2:4-Dihydroxybenzophenone and MeI-MeOH-KOH give 2-hydroxy-4-methoxy-3-methylbenzophenone, m.p. 125° (cf. Jones *et al.*, A., 1932, 852), which affords the 2:4-(OH)₂-compound and 7-methoxy-4-phenyl-8-methylcoumarin, m.p. 94—95°.

A. T. P.

Structure and synthesis of bæckeol. G. R. RAMAGE and W. J. I. STOWE (J.C.S., 1940, 425—426; cf. A., 1939, II, 110).—1:2:4:6-C₆H₂Me(OH)₃ and Pr²CN with ZnCl₂-HCl-Et₂O at room temp. give 2:4:6-trihydroxy-3-methylisobutyrophenone, m.p. 160—161° (+H₂O) or 161—162° (anhyd.), converted

by CH₂N₂-Et₂O into its 4:6-Me₂ ether, m.p. 102—103° (acetate, m.p. 73°), identical with bæckeol.

A. T. P.

Acetylation of α -bromo-ketones and their derivatives. R. P. BARNES and V. J. TULANE (J. Amer. Chem. Soc., 1940, 62, 894—896).—Fused KOAc in boiling Ac₂O is a powerful acetylating agent. It converts CHPhBr·CO·COPh (I) or CHBrBz₂ (II) into $\alpha\beta$ -diacetoxy- α -benzoyl- β -phenylethylene (III), m.p. 133°, and CHPhBzBr (IV), benzoin or its acetate (V) into (CPh·OAc)₂ (VI). KOAc-AcOH has no effect on (I), (II), or (V), converts (IV) into (V), and hydrolyses (III) to CHBz₂·OAc. In cold, conc. H₂SO₄, (III) gives the oily, unstable di-enol, OH·CPh·C(OH)·COPh, which in air yields CO(COPh)₂. Boiling AcOH hydrolyses (VI) to (V); alkali or conc. H₂SO₄ gives benzoin. Metathesis of Br for Ac precedes further acetylation.

R. S. C.

Elimination of methyl from *o*-methoxyacetophenone and action of potassium hydrogen carbonate on resacetophenone and its derivatives. K. OKAZAKI (J. Pharm. Soc. Japan, 1939, 59, 190—193).—5-Methoxy-6-acetyl-2-methylcoumarone-1-carboxylic acid is converted by NH₂Ph, HI and NH₂Ph at 95° into 5-hydroxy-6-acetyl-2-methylcoumarone, m.p. 112°. *p*-OH·C₆H₄·CH₂·CN is acetylated to *p*-acetoxyphenylacetone nitrile, m.p. 49—50°, transformed (Fries) into 4-hydroxy-3-acetylphenylacetone nitrile (I), m.p. 106° (semicarbazone, m.p. 218—219°). This is converted by MeI-K₂CO₃ in boiling COMe₂ into the 4-OMe-compound, m.p. 85—86°, which is demethylated to (I) by NH₂Ph, HI and NH₂Ph at 95°. 1:2:3:4-C₆H₂Ac(OMe)₃ is similarly converted into 2:1:3:4-OH·C₆H₂Ac(OMe)₂, m.p. 83°. 2:6:4:1-(OMe)₂C₆H₂Me·CO₂Me, AlCl₃, and AcCl yield Me 3-hydroxy-5-dimethoxy-2-acetyl-*p*-toluate, m.p. 123°, methylated to the 3:5-(OMe)₂-compound (II), m.p. 92° (semicarbazone, decomp. 215°). β -Orcinol and MeCN afford 3:6-dimethylresacetophenone, m.p. 153°, methylated to the Me₂ ether (III), b.p. 115—118°/3 mm. (semicarbazone, decomp. 206.5°). (II) and (III) give only traces of phenolic compounds when treated with NH₂Ph, HI and NH₂Ph. The Fries transformation of orcinol diacetate leads to 2:6-diacetylorsinol, m.p. 97° (semicarbazone, decomp. 215°), with a minor quantity of isoacacetophenone, both of which are converted by KHC₂O₃ in a sealed tube at 180—190° into *p*-orsellinic acid. Under similar conditions resacetophenone is converted into 6-hydroxy-9-methylfluorone, decomp. 238° (oximino-compound, m.p. 200°), converted by NaOAc and boiling Ac₂O into 3:6-diacetoxyxanthone, m.p. 205°.

H. W.

Stereochemistry of monocyclic rings. I. Interconversion of methylcyclohexane into methylcycloheptane ring and synthesis of 4-methylcycloheptanone. M. QUDRAT-I-KHODA and S. K. GHOSH (J. Indian Chem. Soc., 1940, 17, 19—31).—4-Methylcyclohexanone (I) and aq. NaHSO₃-SO₂ yield the H sulphite compound, converted by aq. KCN at 0° into 1-cyano-4-methylcyclohexanol (II), b.p. 65—68°/5 mm., also prepared, but less pure, from (I) and liquid HCN (+NPhMe₂). (II) and SOCl₂ in C₆H₅N, but better in dry C₆H₆, afford 1-cyano-4-methyl- Δ^1 -cyclohexene (III), b.p. 98—100°/5

mm., hydrolysed by boiling conc. HCl to 4-methyl- Δ^1 -cyclohexene-1-carboxylic acid, m.p. 132—133°, or by conc. H_2SO_4 at room temp. to the corresponding amide, m.p. 140°. (III) and $\text{Na-C}_5\text{H}_{11}\text{OH}$ at 160—170° afford 4-methylcyclohexylmethylamine (IV), b.p. 85—98°/34—35 mm. [Bz derivative, m.p. 93°; hydrochloride, m.p. 248—250° (decomp.; shrinks from 220°); platinichloride, m.p. 248° (decomp.)], and probably di-4-methylcyclohexylmethylamine, b.p. 155—165°/30—35 mm. (IV) and aq. $\text{NaNO}_2\text{-AcOH}$ at 100° (bath) give (?) 4-methylcyclohexylcarbinol, 1-methyl- Δ^4 -cycloheptene, b.p. 69—70°/38 mm. (oxidised by aq. KMnO_4 to γ -methylpimelic acid, m.p. 56°), and 4-methylcycloheptanol, b.p. 105—106°/39—40 mm. (purified through the *H* phthalate, m.p. 95—97°); the latter and $\text{CrO}_3\text{-AcOH}$ at room temp. for 10 days afford 4-methylcycloheptanone (A) [semicarbazones, m.p. 159° (V) (mainly), and m.p. 124°]. Et α -cyano- β -methylsuccinate, b.p. 148—150°/4 mm. (improved prep.), is converted by boiling conc. HCl into β -methylsuccinic acid, the Et ester, b.p. 106°/11 mm., of which with Na-EtOH at 140° (bath) affords β -methylbutane- $\alpha\delta$ -diol, b.p. 120—122°/8 mm., converted by HBr at 140—145° (bath) into $\alpha\delta$ -dibromo- β -methylbutane (VI), b.p. 125—128°/55 mm. This with $\text{CHNa}(\text{CO}_2\text{Et})_2\text{-C}_6\text{H}_6$ affords Et_2 3-methylcyclopentane-1:1-dicarboxylate, b.p. 120—122°/9—10 mm., and thence (aq. KOH-EtOH) the -dicarboxylic acid, m.p. 117—118° (decomp.) (Ag salt). The latter at 185—190° yields the -l-carboxylic acid, b.p. 92—94°/7—8 mm. (Ag salt). (VI) and KCN-EtOH afford β -methyladiponitrile, b.p. 138—140°/30 mm., converted by HCl into β -methyladipic acid [Et ester (VII), b.p. 130—132°/14 mm.], also obtained from 4-methylcyclohexanol and aq. KMnO_4 at 100° (bath). (VII) and Na-EtOH give γ -methylhexane- $\alpha\epsilon$ -diol, b.p. 158—160°/15 mm., whence (as above) $\alpha\epsilon$ -dibromo- γ -methylhexane, b.p. 145—148°/55—60 mm., γ -methylsuberonitrile, b.p. 160—164°/20 mm., and γ -methylsuberic acid, m.p. 146°. Its Ca salt and Fe, distilled in dry N_2 , at 300—350° afford (A), b.p. 105—110°/45—50 mm. [semicarbazone (V)], also obtained from (I) and CH_2N_2 . A. T. P.

3-Methyl-2-hexyl- Δ^2 -cyclopentenone. L. J. BRUSOVA and S. KORE (J. Appl. Chem. Russ., 1939, 12, 1457—1461).—Heptaldehyde is reduced (Raney Ni in EtOH, at 55°) to heptanol (98% yield). Mg heptyl bromide with laevulic acid yields γ -methyl- γ -undecolactone, b.p. 140—140.5°/3 mm., which when heated with H_3PO_4 gives 3-methyl-2-hexyl- Δ^2 -cyclopentenone. R. T.

Polymethylbenzenes. XXV. Reaction between dimethylacrylic acid and the trimethylbenzenes. L. I. SMITH and W. W. PRICHARD (J. Amer. Chem. Soc., 1940, 62, 771—777; cf. A., 1939, II, 306).— $\text{CMe}_2\text{CH}\cdot\text{CO}_2\text{H}$ (I), ψ -cumene (II), and AlCl_3 at -10° give β -3:4:5-trimethylphenylisovaleric acid (III) (50—60%), m.p. 111—112° (Me ester, b.p. 130—130.5°/6 mm.), with some durenene and other acids, rearrangement occurring. (III) is sole product from 1:2:3- $\text{C}_6\text{H}_3\text{Me}_3$ (IV), (I), and AlCl_3 at -10° . Oxidation of (III) by KMnO_4 in aq. KOH gives only α -3:4:5-tricarboxyphenylisobutyric acid, m.p. 192—194° (Me₂ ester, an oil). 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}_4\text{COMe}$

and MgMeI in $\text{Et}_2\text{O-N}_2$ give an oily carbinol; the derived (HCl-light petroleum) chloride is condensed with $\text{CHNa}(\text{CO}_2\text{Et})_2$, hydrolysed to the dicarboxylic acid, m.p. 143.5—148.5° (decomp.), and then decarboxylated at 160° to yield β -2:4:5-trimethylphenylisovaleric acid, m.p. 79—81°, which is partly isomerised to (III) by AlCl_3 . $\text{CMe}_2\text{CH}\cdot\text{COCl}$ (V), (IV), and AlCl_3 at -10° give 2:3:4-trimethyl- β -isopropylideneacetophenone, b.p. 138—139°/6 mm., oxidised by KMnO_4 to 1:2:3:4- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ and cyclised by $\text{AlCl}_3\text{-HCl}$ in CS_2 to 3:3:5:6:7-pentamethylhydrindone, m.p. 103.5—104° (oxime, m.p. 196—196.5°), which is obtained in 99% yield from (III) by conc. H_2SO_4 at room temp. (II), (V), and AlCl_3 in CS_2 give 2:4:5-trimethyl- β -isopropylideneacetophenone (VI), b.p. 131—131.5°/6 mm., oxidised to 1:2:4:5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ and cyclised to 3:3:4:5:7-pentamethylhydrindone, m.p. 54—55.5°. Addition of Br to (I), conversion by $\text{PCl}_5\text{-C}_6\text{H}_6$ into the Br_2 -chloride, b.p. 77—82° (some decomp.)/5 mm., and condensation with (II) by $\text{AlCl}_3\text{-CS}_2$ gives $\alpha\beta$ -dibromo-2:4:5-trimethylisovalerophenone, m.p. 74—76°, also obtained from (VI) by $\text{Br-Et}_2\text{O}$, and cyclised by AlCl_3 to 2-bromo-3:3:4:5:7-pentamethylhydrindone, m.p. 102—104°. *p*-Xylene, (I), and AlCl_3 at 0° give mainly (? 2:5-)dimethylphenylisovaleric acid, m.p. 108—110°, cyclised to (? 3:3:4:7-)tetramethylhydrindone, m.p. 52—53°. *s*- $\text{C}_6\text{H}_3\text{Me}_3$ gives similarly a β -dimethylphenylisovaleric acid, m.p. 110—111°, cyclised to a tetramethylhydrindone, m.p. 62—63°. Mesityl oxide with (II) and AlCl_3 at 0° gives 1:1:3:4:5:7-hexamethylindene, m.p. 87.5—88.5°, but with PhOH , ψ -cumenol, or *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$ in conc. H_2SO_4 or $\text{H}_2\text{SO}_4\text{-AcOH}$ at 0° , *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH-AlCl}_3$, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OMe-PhNO}_2\text{-AlCl}_3$, or *p*- $\text{C}_6\text{H}_4(\text{OMe})_2\text{-AlCl}_3\text{-CS}_2$ gives no identifiable product. *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ and $\text{MgMeI-Et}_2\text{O}$ give a carbinol, m.p. 43—44°, converted by HCl and CaSO_4 in C_6H_6 into a halogen-free substance, m.p. 95—96°. R. S. C.

3:3:5:6:7-Pentamethylhydrindone and 4:4:5:6:8-pentamethylhydrocarbostyryl. L. I. SMITH and W. W. PRICHARD (J. Amer. Chem. Soc., 1940, 62, 778—780).—Beckmann rearrangement ($\text{PCl}_5\text{-POCl}_3$) of 3:3:5:6:7-pentamethylhydrindone oxime gives only mixtures. 3:3:5:6:7-Pentamethylhydrindone gives ($\text{NaNO}_2\text{-H}_2\text{SO}_4\text{-CHCl}_3$; -5°) mainly the 4- NO_2 , m.p. 94—94.5°, and thence (Zn dust-AcOH) the 4- NH_2 , double m.p. 84° and 101—102°, and ($\text{NaNO}_2\text{-10% H}_2\text{SO}_4$; CuSO_4) the 4-OH-derivative, m.p. 183—185° (oxime, m.p. 183—185°, with $\text{PCl}_5\text{-POCl}_3$ gives an amorphous solid). 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}_3\text{NH}_2$ and $\text{CMe}_2\text{CH}\cdot\text{COCl}$ in hot C_6H_6 give the amide, m.p. 107.5—108°, cyclised by AlCl_3 at 100° to 4:4:5:6:8-pentamethylhydrocarbostyryl, m.p. 209—210°, which resists hydrolysis by $\text{Ba}(\text{OH})_2$ at 150—250°. R. S. C.

Synthesis of 1-keto-2:3-dimethylnaphthindene. E. F. ARCANGELI (R. C. Atti Accad. Ital., 1939, [vii], 1, 55—59).—2- $\text{C}_{10}\text{H}_7\text{Ac}$ (I) and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ with Zn in C_6H_6 give, after treatment with H_2SO_4 , (I) and Et β -hydroxy- β -2-naphthyl- α -methyl-n-butyrate, b.p. 275—280°/62 mm., which when heated with P_2O_5 for 2 hr. gives 1-keto-2:3-dimethyl- α (or β)-naphthindene (II), m.p. 129.5—130°, b.p.

229—230°/34 mm. With conc. H_2SO_4 , crude (II) gives (I). E. W. W.

Preparation of substituted ketimines. R. CANTAREL (Compt. rend., 1940, 210, 403—405).— COPh_2 vapour with NH_3 in presence of ThO_2 at 380° gives CPh_2NH (I), b.p. 160°/13 mm. Many aldehydes and ketones in EtOH saturated with NH_3 containing Ni at 70° (under 8—9 kg. per sq. cm. H_2 pressure) give the corresponding amines in high yield, but COPh_2 gives only traces of CHPh_2OH and CHPh_2NH_2 ; the latter is formed quantitatively by reducing (I) (H_2). Equimol. amounts of (I) and primary amines give NH_3 and the appropriate imine. The following are new: *benzhydrylidene-β-phenylethylamine*, m.p. 35°, and *-cyclohexylamine*, m.p. 49°. $\text{CPh}_2\text{N}\cdot\text{CHPh}_2$ with H_2 -catalyst gives *dibenzhydrylamine* (~100%), m.p. 143°. J. L. D.

Steroid ketones.—See B., 1940, 404, 405.

Sterols. XCVII. **Sarsasapogenin.** R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 900—902).—Sarsasapogenin acetate with MgEtBr in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ gives a *diol*, $\text{C}_{29}\text{H}_{50}\text{O}_3$, m.p. 159—161.5° [*diacetate* (I), m.p. 87.5—89°], and with MgMeI gives a *diol*, $\text{C}_{28}\text{H}_{48}\text{O}_3$, m.p. 179—181.5° (*di-p-nitrobenzoate*, m.p. 192—194°). CrO_3 in ~90% AcOH at 90° oxidises (I) to a product, hydrolysed (NaOH) to 3-hydroxyatiobilanic acid. The Me_2 ester thereof with aq. $\text{MeOH}-\text{NaOH}$ (1 mol.) gives the Me_1 ester, m.p. 211—213°, the *acetate*, m.p. 181.5—183.5°, of which gives an oily chloride, converted by CH_2N_2 into a *diazo-ketone*, $\text{C}_{23}\text{H}_{33}\text{O}_5\text{N}_2$, m.p. 159—160° (decomp.). Ag_2O in EtOH at 70—80° then gives an oil, which by hydrolysis, acetylation, heating (250°), and hydrolysis gives *atiocholan-3(β)-ol-17-one* (II), *form*, m.p. 117—119°. Identity of (II) with the product of Ruzicka *et al.* (*form*, m.p. 151—152°, A., 1934, 1221) is proved by prep. of the semicarbazone, m.p. 241—242.5° (decomp.), and reduction by $\text{Na}-\text{C}_5\text{H}_{11}\text{OH}$ to *atiocholane-3(α):17(α)-diol* (III). Partial hydrolysis ($\text{MeOH}-\text{KOH}$) of the *diacetate* of (III) followed by oxidation (CrO_3) and hydrolysis gives (mainly) *atiocholan-17-ol-3-one*, m.p. 139—141°, which with $\text{Br}-\text{HBr}-\text{AcOH}$ affords a product converted by boiling $\text{C}_5\text{H}_5\text{N}$ into testosterone. R. S. C.

Sterols. XCV. **Acid isomerisation of ψ-sapogenins to sapogenins.** R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1940, 62, 896—898).—Clemmensen reduction of ψ-sarsasapogenone gives deoxysarsasapogenin. $\text{HCl}-\text{EtOH}$ at 25° converts ψ-sarsasapogenin, ψ-tigogenin, and ψ-chlorogenin into sarsasapogenin, tigogenin, and chlorogenin, respectively, but has no effect on dihydro-ψ-sarsasapogenin. The naturally occurring saponin glucosides may be derived from the ψ-forms or the keto-diol form, e.g., $\begin{matrix} \text{CMc}\cdot\text{CHR} \\ | \\ \text{CH}-\text{CH}_2 \end{matrix} > \text{CH}\cdot\text{OH}$ ($\text{R} = \text{CHMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$). R. S. C.

Total synthesis of the sex hormone, equilenin, and its stereoisomerides. W. E. BACHMANN, W. COLE, and A. L. WILDS (J. Amer. Chem. Soc., 1940, 62, 824—839).—Equilenin (I) and three stereoisomerides thereof are synthesised. Results already reported (A., 1939, II, 261) are amplified, the following

being new. Prep. of 6:1- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (from the Ac derivative), 6:1- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot[\text{CH}_2]_2\cdot\text{OH}$ [76—84% from 1:6- $\text{C}_{10}\text{H}_6\text{I}\cdot\text{OMe}$, EtBr , Mg , and $(\text{CH}_2)_2\text{O}$ in $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$], 6:1- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot[\text{CH}_2]_2\cdot\text{Br}$ (I) (by $\text{PBr}_3-\text{C}_6\text{H}_6$), 6:1- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ (II) [75—89% from (I), $\text{CH}_3(\text{CO}_2\text{Et})_2$, NaOEt , etc.], and 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene (III) [90—95% from (II) by $\text{SOCl}_2-\text{C}_5\text{H}_5\text{N}-\text{Et}_2\text{O}$, followed by $\text{SnCl}_4-\text{C}_6\text{H}_6$] is modified. $\text{Me}_2\text{C}_2\text{O}_4$, (III), and NaOMe in C_6H_6 give *Me* 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene-2-glyoxylate, m.p. 138—140° (Pyrex) or 134—135° (soda glass), converted at 180°, best when mixed with powdered glass, into *Me* 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene-2-carboxylate, double m.p. 110—111° (nearly completely) and 125—126.5°, and thence by $\text{MeI}-\text{NaOMe}-\text{MeOH}$ into the 2-Me derivative (IV), m.p. 84.5—85°. Hydrolysis of (IV) by aq. $\text{MeOH}-\text{KOH}$ affords 1-keto-7-methoxy- (V), m.p. 109—110°, which with 42% HBr gives 7-hydroxy-1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene, m.p. 193—196° (air), 195.5—197.5° (after resolidification, 197—197.5°; vac.). With Zn , I , and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$ in $\text{C}_6\text{H}_6-\text{Et}_2\text{O}$, (IV) gives *Me* 1-hydroxy-2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-acetate (85—90%), m.p. 125—125.5° [hydrolysed by alkali to (V)], which with $\text{SOCl}_2-\text{C}_5\text{H}_5\text{N}$ (with or without C_6H_6), followed by $\text{KOH}-\text{MeOH}$, gives the *anhydride* (VI), m.p. 233—234°, of *syn*-2-carboxy-7-methoxy-2-methyl-1:2:3:4-tetrahydro-1-phenanthrylideneacetic acid and the *anti-acid* (VII), m.p. 216—217° (gas) (Me_2 ester, m.p. 113.5—114°). Na-Hg in aq. KOH then gives α- (VIII) (45%), m.p. 231—232°, and β-2-carboxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-acetic acid (IX) (55%), m.p. (+ C_6H_6) ~145° or 150°, (anhyd.) 213—214°, obtained similarly in 33 and 43% yield, respectively, from (VI) or in 44—47 and 40—43% yield, respectively, without isolation of the unsaturated compounds. The Me_2 ester, m.p. 114—115.5°, of (IX) is hydrolysed by N-NaOH (1 mol.) in hot MeOH to the 2-carbomethoxy-1-acetic acid, m.p. 211—212°, converted (Arndt-Eistert) into *Me* β-2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-propionate, m.p. 101—102°. Cyclisation by NaOMe in $\text{C}_6\text{H}_6-\text{N}_2$ then yields 97% of 16-carbomethoxy-dl-equilenin *Me ether*, m.p. 181—182° (vac.; after softening), converted by boiling $\text{HCl}-\text{AcOH}-\text{H}_2\text{O}-\text{N}_2$ into dl-equilenin (X), m.p. 276—278° (vac.) [once 287—288° (vac.)], sometimes 265°] [*benzoate*, m.p. 248.5—249.5° (vac.); *acetate*, m.p. 153—154° (159.5—160° after resolidification; vac.)], and its *Me ether*, m.p. 185—186.5° (vac.) [converted by MgMeI , followed by KHSO_4 at 160—170°, into 7-methoxy-3':3'-dimethyl-1:2-cyclopentenophenanthrene (XI)]. Esterification of (X) in dioxan- $\text{C}_5\text{H}_5\text{N}-\text{N}_2$ and crystallisation gives d-equilenin 1-menthoxyacetate (XII), m.p. 174—174.5°, [α]_D²⁰ +18° in C_6H_6 , hydrolysed to d-equilenin, which is proved to be identical with the natural product by means of 6 derivatives [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 206—207° (corr.)], absorption spectrum, and physiological action. l-Equilenin, m.p. 250—251° (vac.), 258—259° (vac.; corr.), [α]_D²⁰ -85° in dioxan [d-menthoxyacetate (XIII), m.p. 174.5—175° (vac.), [α]_D²⁰

—16° in C_6H_6], is obtained similarly from (X) or the residues from (XII) (after hydrolysis). A 1:1 mixture of (XII) and (XIII) has m.p. 151—152° (vac.). By similar methods (VIII) gives *Me* 2-carbomethoxy-7-methoxy-1:2:3:4-tetrahydrophenanthryl-1-acetate, dimorphic, m.p. 86—89° and 126—126.5°, the 2-carbomethoxy-1-acetic acid (XIV), m.p. ~110—112° (gas) and then 137—138°, α -2-carboxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-propionic acid, m.p. 89—89.5°, 16-carbomethoxy-dl-isoequilenin *Me* ether, m.p. 149—149.5° (air), 152.5—153.5° (vac.), dl-isoequilenin *Me* ether, m.p. 127—127.5° (vac.), 130—130.5° (vac.) after resolidification [gives (XI) in 3% yield], and dl-isoequilenin, m.p. 223—224° (vac.) [acetate, m.p. 159—160° (vac.); s - $C_6H_3(NO_2)_3$ compound, m.p. 186—187° (vac.)]. (XIV) gives 1-menthyl 1- α -2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-acetate (XV), m.p. 139.3—139.8°, $[\alpha]_D^{20}$ —152° in C_6H_6 , converted into the *Me*₂ ester, m.p. 110—110.3°, $[\alpha]_D^{20}$ —151° in C_6H_6 , and *Me* *H* ester, m.p. 130°, 159—160° after resolidification, of the *l*-acid and thence into *Me*₂ 1- α -2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-propionate, m.p. 103—103.5°, 16-carbomethoxy-*d*-isoequilenin, m.p. 147—150°, and *d*-isoequilenin, m.p. 257—258° (vac.), 265—266° (vac.; corr.), $[\alpha]_D^{20}$ +147° in dioxan, +173° in abs. EtOH [Me ether, m.p. 118.5—119.5°; acetate, dimorphic, m.p. 146—147° (vac.) (149—149.5°) and 127—128°, $[\alpha]_D^{20}$ +137 ± 7°, +129.4° in abs. EtOH], identical with 14-epiequilenin (Hirschmann *et al.*, A., 1939, II, 76). Hydrolysis (KOH-MeOH) of the residues after separation of (XV) and methylation (CH_2N_2) gives *Me* *dl*-, m.p. 125.5—126°, and *d*- α -2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-acetate, m.p. 108—109° or 110—110.5°, *Me* *d*- α -2-carbomethoxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-propionate, m.p. 103—103.5°, $[\alpha]_D^{20}$ +122°, and *l*-isoequilenin, dimorphic, m.p. 272—273° (vac.) and 257—258° (vac.), $[\alpha]_D^{20}$ —147° in dioxan, —162° in abs. EtOH. Oestrogenic units are *d*-30 and *l*-equilenin 400, *d*- and *l*-isoequilenin >500 μ g.

R. S. C.

Hydroxyquinones. I. Synthesis of dyes of the polyporic acid series. M. ASANO and Y. KAMEDA (J. Pharm. Soc. Japan, 1939, 59, 291—293).— p - $C_6H_4Me \cdot N_2Cl$ with NaOAc and *p*-benzoquinone (I) in EtOH at <5° yields 2-mono- (II), m.p. 137—139°, and 2:3:5-tri-*p*-tolyl-*p*-benzoquinone, m.p. 197—199°. 2-Phenyl-*p*-benzoquinone and PhMe or (II) and C_6H_6 with $AlCl_3$ yield 2-phenyl-5-*p*-tolylbenzoquinone, m.p. 171—173°, reduced (Zn-AcOH) to 2-phenyl-5-*p*-tolylquinol, m.p. 151—153°, the 3:6- Br_2 -derivative, m.p. 195—197° (prep. in $CHCl_3$), of which is hydrolysed by 10% MeOH-KOH to 3:6-dihydroxy-2-phenyl-5-*p*-tolylbenzoquinone, m.p. 246—248°. p -OMe- $C_6H_4 \cdot N_2Cl$ and (I) similarly give 2-anisyl-*p*-benzoquinone, m.p. 112—113°, which with C_6H_6 and $AlCl_3$ yields 2-phenyl-5-*p*-anisylbenzoquinone, (III), m.p. 177—183° (corresponding quinol, m.p. 157—158°). With NH_2Et in EtOH, (III) in EtOAc yields 3:6-di(ethylamino)-2-phenyl-5-anisylbenzoquinone, m.p. 256°, which is hydrolysed by 50% H_2SO_4 to 3:6-dihydroxy-2-phenyl-5-anisylbenzoquinone, m.p. 261—263°.

J. D. R.

Constitution and synthesis of embelin. M. ASANO and K. YAMAGUTI (J. Pharm. Soc. Japan, 1940, 60, 34—38, and Proc. Imp. Acad. Tokyo, 1940, 16, 36—38).—Contrary to Hasan *et al.* (A., 1931, 1158) embelin (I) is 3:6-dihydroxy-2-undecyl-*p*-benzoquinone (II), and not the dodecyl derivative (III). In this series identification by the method of mixed m.p. is untrustworthy and the identity of (I) with synthetic (II) is established by the Debye-Scherrer diagrams. 3:4:5-(OMe)₃ $C_6H_2 \cdot CO \cdot CH_2 \cdot CO_2Et$ is condensed with $C_{10}H_{21}I$ and NaOEt in EtOH to *Et* α -3:4:5-trimethoxybenzoyl-laurate, m.p. 46°, which does not give a colour with $FeCl_3$ in EtOH and is converted by boiling 1% KOH-EtOH into 3:4:5-trimethoxylauropenone, m.p. 65° (*p*-nitrophenylhydrazones, m.p. 96°). This is reduced by Na-boiling $C_5H_{11} \cdot OH$ to 3:5-dimethoxydodecylbenzene, b.p. 165°/0.3 mm. (demethylated to 3:5-dihydroxydodecylbenzene, m.p. 81°), which is oxidised ($Na_2Cr_2O_7$ in AcOH at 85—90°) to 6-methoxy-2-dodecyl-*p*-benzoquinone (IV), m.p. 74°. NH_2Me in EtOH at 0° transforms (IV) into 3:6-di(methylamino)-2-dodecyl-*p*-benzoquinone, m.p. 147°, which is converted by 50% H_2SO_4 at 100° into 3(or 6)-methylamino-6(or 3)-hydroxy-2-dodecyl-*p*-benzoquinone, m.p. 163—164°; this with boiling 50% H_2SO_4 -AcOH yields (III), m.p. 142° (dibenzoate, m.p. 96—96.5°), which does not depress the m.p. of (I), from which it differs in Debye-Scherrer diagram. Reductive acetylation of (III) affords 2:3:5:6-tetra-acetoxydodecylbenzene, m.p. 120°. Tridecoic acid, m.p. 39.5° (*p*-toluidide, m.p. 87.5—88°), is obtained by oxidation of (III) with H_2O_2 and dil. KOH. 3:4:5-(OMe)₃ $C_6H_2 \cdot CO \cdot CH_2 \cdot CO_2Et$ and $C_9H_{19}I$ afford *Et* α -3:4:5-trimethoxybenzoylundecate, m.p. 39—40°, and thence successively 3:4:5-trimethoxyundecophenone, m.p. 51—52°, 3:5-dimethoxyundecylbenzene, b.p. 170°/1 mm. (3:5-dihydroxyundecylbenzene, m.p. 69—71°), 6-methoxy-, m.p. 78—79°, and 3:6-di(methylamino)-, m.p. 147—148°, -2-undecyl-*p*-benzoquinone, and (II), m.p. 143—144° (dibenzoate, m.p. 97°). 2:3:5:6-Tetra-acetoxundecylbenzene has m.p. 124°.

H. W.

2-Acetoxymethyl-1:4-naphthaquinone, m.p. 110°, and -naphthalene, m.p. 61°; 2-methyl-naphthaquinone monoxime, m.p. 165°.—See A., 1940, III, 431.

Compounds having antihæmorrhagic activity. L. F. FIESER, M. TISHLER, and W. L. SAMPSON (J. Amer. Chem. Soc., 1940, 62, 996).—Application of the vitamin- K_1 synthesis (A., 1940, II, 96) gives 2-geranyl-, 2-farnesyl, and 2-phytyl-1:4-naphthaquinone (I) [all have -*K*-activity, (I) fully at 50 μ g.], 2:3:5-trimethyl-6-phytylbenzoquinone, an oil (no -*K*-activity; quinol diacetate, m.p. 56°; with $SnCl_2$ -AcOH-HCl gives α -tocopherol), 2-methyl-3-phytyl-5:8-dihydro-1:4-naphthaquinone (active at 5—6 μ g.). - K_1 gives the $\beta\gamma$ - H_2 -derivative (active at 6 μ g.; quinol diacetate, m.p. 57—58°) and $\beta\gamma$:5:6:7:8- H_6 -derivative (slightly active; quinol diacetate, m.p. 53°). 2-Methyl-5:8-dihydro-1:4-naphthaquinol and the adduct from toluquinone and $(CH_2 \cdot CH)_2$ are active at 8- μ g. doses. A by-product in the synthesis of - K_1 is a ketone, $C_{31}H_{48}O_2$ (absorption max. at 253 and 300 $m\mu$.; 2:4-dinitrophenylhydrazones, m.p. 107—

108°; 1 active H), active at 50 μ g., which is reduced by $\text{Al}(\text{OPr}^i)_3$ to a diol, (?) $\text{C}_{31}\text{H}_{52}\text{O}_2$, and by pyrolysis gives a little $-K_1$. The isomeric *naphthotocopherol* (absorption max. at 246 and 320 μ ; p -nitrobenzoate, m.p. 84–85°) is active at 3×10^{-4} -g. doses and gives on oxidation a *OH-quinone*. 2-Methyl-3-farnesyl-1:4-naphthaquinone is less active than $-K_1$. R. S. C.

Action of nitric acid on anthracene. IV. [Nitroanthraquinones.] R. ODA (J. Soc. Chem. Ind. Japan, 1940, 43, 14–15B).—2:7-Dinitro- (I) is separated from 2-nitro-anthraquinone by dissolution in $\text{NaOH}-\text{COMe}_2$, but cannot be recovered therefrom. Hot, aq. Na_2SO_3 , best with $\text{C}_5\text{H}_5\text{N}$, converts (I) into the 2-NH- SO_3Na derivative. When a mixture of (I) and anthraquinone is boiled in NH_2Ph for 10 min. and then cooled, both solids separate, but, if boiling is continued for 3–4 hr. (also in $p\text{-C}_6\text{H}_4\text{Me}-\text{NH}_2$ containing a little $\text{C}_5\text{H}_5\text{N}$), the (I) remains in solution as a mol. compound and is recovered by HCl .

R. S. C.

1-Amino-2-methylanthraquinone in relation to phthaloylation and Schiff's base. G. B. CRIPPA (Atti X Congr. Internaz. Chim., 1938, IV, 842–850).—Largely an account of work previously abstracted (A., 1939, II, 181, 379). Condensation of 1-amino-2-anilomethylanthraquinone with COPhMe affords a substance, m.p. 130–135°, probably (I).

F. O. H.

1:3:8-Trihydroxyanthraquinone. W. K. ANSLOW, J. BREEN, and H. RAISTRICK (J.C.S., 1940, 427–428).—Emodic acid (see A., 1940, II, 135) is decarboxylated by quinoline-Cu chromite at 225–230° in O_2 -free N_2 to 1:3:8-trihydroxyanthraquinone, new m.p. 287–288°, purified through its triacetate, new m.p. 194–195°. Methylation ($\text{Me}_2\text{SO}_4-\text{COMe}_2-2\text{N}-\text{NaOH}$) gives 1:3:8-trimethoxyanthraquinone, m.p. 195–196°.

A. T. P.

Constitution of carviolin, a colouring matter of *Penicillium carmino-violaceum*. Biourge. H. G. HEND (Biochem. J., 1940, 34, 577–579).—Demethylation of carviolin (I) (A., 1940, II, 99) with $\text{HBr}-\text{AcOH}$ yields a Br_1 -compound, $\text{C}_{15}\text{H}_9\text{O}_5\text{Br}$, m.p. 248°, which with aq. $\text{AcOH}-\text{AgOAc}$ gives demethyl-carviolin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, m.p. 278–280°. Methylation of (I) yields a Me_3 ether, m.p. 186°, identical with ω -hydroxyemodin Me_4 ether, indicating that (I) is an ω -hydroxyemodin Me_1 ether. Successive oxidation (Pb_3O_4 in conc. H_2SO_4) and reduction ($\text{SO}_2-\text{H}_2\text{O}$) of (I) gives a compound showing the absorption bands of a 1:4:5:8-tetrahydroxyanthraquinone.

P. G. M.

Elimination reactions and their steric course. W. HÜCKEL, W. TAPPE, and G. LEGUTKE (Annalen, 1940, 543, 191–230; cf. A., 1939, II, 147).—*l*-Menthyl *p*-toluenesulphonate (I) and $\text{EtOH}-\text{NaOEt}$ afford (cf. A., 1939, II, 120) *trans*- Δ^2 -menthene (II), b.p. 55.5°/16 mm., which has $\alpha_D +107^\circ$, $[\alpha]_D^{20} +132.1^\circ$ (cf. Read *et al.*, A., 1939, II, 79), when carefully fractionated (over Na ; reduced pressure in N_2). The oxide, b.p. 83–84°/17 mm., from (II) and BzO_2H in CHCl_3 , is converted by 5% HClO_4 into the very

viscous menthanediol, $[\alpha]_D^{20} +33^\circ$ in EtOH , which is oxidised (cold aq. $\text{KMnO}_4 + \text{K}_2\text{CO}_3$) to a lactonic acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, m.p. 192° (sinters 182°), and non-cryst. material. Δ^3 -Menthene (III) is rapidly racemised by boiling $\text{EtOH}-p\text{-C}_6\text{H}_4\text{Me}-\text{SO}_3\text{H}$ whilst (II) is similarly little affected; (III) is also oxidised much more rapidly than (II) by BzO_2H (cf. Meerwein *et al.*, A., 1926, 722). These methods are applied to the determination of the amount of (II) in admixture with (III). Thus, *l*-menthyl chloride (IV) and NaOEt give a little (II) [not obtained wholly free from unchanged (IV)]; (I) and EtOH in presence and absence of CaCO_3 afford mixtures, $\alpha +78^\circ$ and $+35^\circ$, respectively, each containing 32% of (II). The amounts of (II) in the mixtures obtained from *d*-neomenthyl chloride and $\text{EtOH}-\text{NaOEt}$, *d*-neomenthylamine (V) and HNO_2 , *l*-menthyl xanthate (thermal decomp.), and *d*-neomenthyl xanthate (prep. described; decomp. at 185–220°) are ~25, 20, 28, and 80%, respectively. Some inactive menthan-4-ol (VI) is also formed from (V) and HNO_2 ; the intermediate *d*-neomenthyl ion presumably rearranges to the *tert*-4-menthyl ion which then adds OH^- [to give (VI)] or eliminates H^+ [forming inactive (III)]. Racemisation of (III) by $\text{EtOH}-p\text{-C}_6\text{H}_4\text{Me}-\text{SO}_3\text{H}$ probably occurs owing to the formation of (VI) (as ester). The possible production of the *l*-menthyl ion from (I) in EtOH , and subsequent loss of H^+ to give (II) and (III) is discussed. The reaction between (IV) and NaOEt is considered to be of the following type: $\text{OEt}^- + \text{H}\cdot\text{CR}_2\cdot\text{CR}_2\text{Cl}$ (H and Cl in *trans* position) $\rightarrow \text{OEt}^- \text{H}^+ \cdots \text{CR}_2\cdot\text{CR}_2 \cdots \text{Cl}^- \rightarrow$

$\text{EtOH} + \text{CR}_2\cdot\text{CR}_2 + \text{Cl}^-$; Tschugaev's xanthate method is held to be strictly analogous, SMe^- reacting as OEt^- . The formation of menthenes and octahydronaphthalenes from (i) menthyl and decahydronaphthyl esters, respectively, in EtOH or $\text{EtOH} + \text{CaCO}_3$, and (ii) the corresponding amines and HNO_2 , is of type *E* 1 (Hughes *et al.*, A., 1937, I, 467). Elimination reactions of type *E* 2 (cf. *loc. cit.*; Hanhart *et al.*, A., 1927, 650) are: (i) the above esters with NaOalk , (ii) exhaustive methylations (above amines), and (iii) thermal decomp. of the xanthates.

The *p*-toluenesulphonate, m.p. 72°, of *trans*-decahydro- α -naphthol, m.p. 49°, with boiling $\text{EtOH}-\text{NaOH}$ gives 90% of *trans*- $\Delta^{1:2}$ -octahydronaphthalene (VII) and 10% of the $\Delta^{1:9}$ -isomide (VIII). The *p*-toluenesulphonate, m.p. 98°, of *trans*-decahydro- α -naphthol, m.p. 63°, similarly affords (VII), whilst the *p*-toluenesulphonate, m.p. 96°, of *cis*-decahydro- α -naphthol, m.p. 93°, yields (VIII). Thermal decomp. of the corresponding xanthates gives approx. 4:1, 1:4, and 9:1 mixtures, respectively, of (VII) and (VIII). *trans*- Δ^2 -Octahydronaphthalene, b.p. 62°/22 mm., new m.p. -14° [oxidised (alkaline KMnO_4) to *trans*-cyclohexane-1:2-diacetic acid], is obtained from the *p*-toluenesulphonates, m.p. 110° and 66°, of *trans*-decahydro- β -naphthol, m.p. 53° and 75°, respectively, with $\text{EtOH}-\text{NaOEt}$ or $\text{Pr}^i\text{OH}-\text{NaOPr}^i$. In many of these reactions with NaOalk a little free decahydronaphthol and alkyl ether are also formed (cf. following abstract). Borneol *p*-toluenesulphonate with $\text{EtOH}-\text{NaOEt}$ gives mainly borneol. Ozonolysis of menthenes of $\alpha +78^\circ$ to $+104^\circ$ in AcOH at 0° affords mainly active "hydroxymenthyl acid" (*semicarbazone*, m.p. 153°, $[\alpha]_D^{21} +4.6^\circ \rightarrow +8^\circ$ in 10% Na_2CO_3). An

inactive *semicarbazone*, m.p. 163°, is obtained from menthenes of $\alpha \sim 30^\circ$. H. B.

Walden inversion. V. Walden inversion in the formation of ethers. W. HÜCKEL and H. PIETRZOK (Annalen, 1940, 543, 230—239; cf. A., 1940, II, 135).—*l*-Menthyl chloride (I) and boiling EtOH + CaCO₃ give some menthene but no menthyl Et ether; with MeOH + CaCO₃ at 180—190° (autoclave)/65 hr., a 27 : 73 mixture of *trans*- Δ^2 - and Δ^3 -menthene and a smaller amount of a 2 : 3 mixture of *l*-menthyl and *d*-neomenthyl Me ether are formed. No ether is obtained from (I) and EtOH-NaOEt but *l*-menthyl *p*-toluenesulphonate gives (cf. A., 1939, II, 120) small amounts of *l*-menthol and *d*-neomenthyl Et ether, b.p. 83—84°/14 mm., $\alpha_D + 26.05^\circ$. Borneol, $\alpha_D + 4.6^\circ$, yields an inactive *p*-toluenesulphonate, m.p. 80.5°, which with boiling EtOH + CaCO₃ affords camphene and a smaller amount of camphene hydrate Et ether, b.p. 86—89°/14 mm. The decahydro- β -naphthyl Et, b.p. 112°/15 mm., and Pr² ethers, b.p. 114°/15 mm., obtained (cf. A., 1940, II, 227) with *trans*- Δ^2 -octahydronaphthalene from the *p*-toluenesulphonate of *trans*-decahydro- β -naphthol, m.p. 53°, are both cleaved by NaEt to *trans*-decahydro- β -naphthol, m.p. 75°, showing that complete Walden inversion has occurred in their formation. Reaction mechanisms are discussed. H. B.

Fenchene series. X. Isomerisation of α -fenchene. G. KOMPPA and G. A. NYMAN (Annalen, 1940, 543, 111—118; cf. A., 1938, II, 371).—Short treatment (7—15 min.) of α -fenchene (I) (*dl*-form used at its b.p.) with KHSO₄ gives β - (II) and γ -fenchene (III); the formation of little or no (I) from fenchyl alcohol and KHSO₄ (or other acidic reagents) is thus partly due to the foregoing isomerisation. Dehydration of 2-methyl- α -fenchocamphorol by distillation affords (I) but KHSO₄ at 150—160° (short time) gives (II) and (III). Contrary to Wallach (A., 1899, i, 65), active (II) ("*D-d*-fenchene"), which contains a variable amount of (III), is not converted by EtOH-H₂SO₄ into pure *l*-(I) ("*D-l*-fenchene"); 2N-H₂SO₄ or KHSO₄ in boiling EtOH gives *l*-(I), *l*-methylsantene, and *isofenchol* Et ether. Structures are proved by oxidation [except for (III) which gives an adduct with PhN₃]. H. B.

Bornyl chloride and its isomerides. I. V. I. LUBOMILOV, B. N. RUTOVSKI, and T. V. SCHEREMETVA (J. Gen. Chem. Russ., 1939, 9, 2067—2074).—The velocity of hydrolysis of bornyl chloride (with KOPh at 200—210°) is \gg that of the liquid chlorides obtained by saturation of *d*-pinene with HCl. Fractionation of the mixture of hydrocarbons obtained by heating the mixture of monochlorides with KOPh gives camphene, limonene, dipentene, isomeric fenchenes, and a new dicyclic terpene, C₁₀H₁₆, b.p. 157.8—158.5°/750 mm., $[\alpha]_D - 7.87^\circ$, the acetate of which is hydrolysed to an alcohol, C₁₀H₁₇OH, b.p. 86—88°/10 mm. (*phenylurethane*, m.p. 88—89°). This is oxidised (CrO₃) to a ketone [*oxime*, m.p. 132.5—133°; *semicarbazone*, m.p. 217—219° (decomp.)]. With HCl it gives a solid hydrochloride, which rapidly liquefies at room temp. R. T.

Lupanetriol and its oxidation. E. R. H. JONES and R. J. HEAKINS (J.C.S., 1940, 456—457).—Lupeol and OsO₄ in Et₂O, followed by decomp. (Na₂SO₃) of the Os complex, give *lupanetriol*, C₃₀H₅₂O₃, m.p. 278—284° (decomp.), $[\alpha]_D^{20} + 2.1^\circ$ in C₅H₅N (*diacetate*, m.p. 174°, $[\alpha]_D^{20} + 4.5^\circ$ in CHCl₃), which is oxidised by Pb(OAc)₄ to *norlupananol*, m.p. 230°, identical with the oxidation product (CrO₃) of lupenyl acetate. This proves the presence of an exocyclic CH₂ in lupeol and betulin. F. R. S.

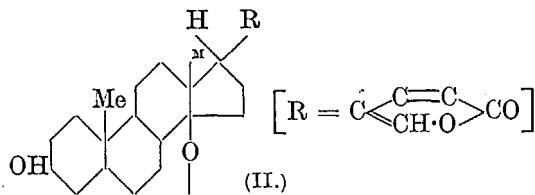
Paprika colouring matter. XI. Isomerisation phenomena. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1940, 543, 248—257; cf. A., 1937, II, 384).—When a solution of chromatographically homogeneous capsanthin (I) in C₆H₆ is kept at $\sim 20^\circ$, some isomerisation of (I) to neocapsanthins A, B, and C occurs; the amounts (determined colorimetrically after chromatographic separation), in the order quoted, after 7 and 13 days are in the ratio 92 : 8 : 0 : 0 and 62 : 16 : 15 : 7, respectively. The neocapsanthins are similarly more labile; A in C₆H₆ at room temp./15 days gives a 54 : 46 mixture of (I) and A, whilst B affords a 50 : 38 : 12 mixture of (I), A, and B. Isomerisation occurs much more readily in boiling C₆H₆; equilibrium mixtures containing ~ 80 and $\sim 65\%$ of (I) are formed from (I) and A, respectively, after 30—45 min. Similar isomerisation of (I) is effected still more rapidly by 1% of I in C₆H₆ at $\sim 20^\circ$. The neocapsanthins are more sol., less cryst., and show absorption at shorter λ ; (I), A, B, and C have $[\alpha]_D$ (in C₆H₆) 0 ± 5 — 10° , $+89^\circ$, $+21 \pm 5^\circ$, and $+27 \pm 10^\circ$, respectively. Acylation of the OH groups of (I) causes a marked change in the tendency for isomerisation and adsorption. Capsanthin dipalmitate (II), new m.p. 95° (corr.), resembles physalene (A., 1940, II, 138); it is converted in boiling light petroleum (b.p. 70°) into $\sim 35\%$ (equilibrium) of the oily neocapsanthin dipalmitates-I and -II. The same equilibrium mixture is also formed with I and also when a mixture of the dipalmitates-I and -II is used. Capsorubin, $[\alpha]_D \pm 0^\circ$ in C₆H₆, resembles (I) and gives neocapsorubins A and B, $[\alpha]_D - 134^\circ$ and -69° in C₆H₆, respectively, whilst its dipalmitate affords neocapsorubin dipalmitates-I and -II. H. B.

Carotenoids of purple bacteria. V. Rhodoviolascene. P. KARRER and H. KOENIG (Helv. Chim. Acta, 1940, 23, 460—468; cf. A., 1936, 248, 340, 1561; 1938, II, 277).—Oxidation of rhodoviolascene (I) with KMnO₄ yields bixindialdehyde and an incompletely identified dialdehyde which is free from OMe; a revision of the formula suggested tentatively for (I) is therefore essential. H. W.

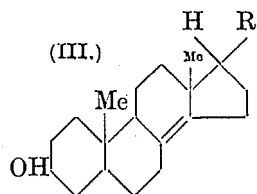
Constituents of Nephromopsis stracheyi, f. ectocarpitma, Hue. III. M. ASANO and M. TANIGUTI (J. Pharm. Soc. Japan, 1939, 59, 216; cf. A., 1935, 863; 1939, II, 97).—Chromatography (Al₂O₃) of acid B (*loc. cit.*) results in the isolation of *l*-protolichesteric acid, m.p. 103—106°, $[\alpha]_D^{20} - 12.4^\circ$, converted by CH₂N₂ into the pyrazoline derivative, C₂₁H₃₆O₄N₂, m.p. 60—61°, $[\alpha]_D^{20} - 288.2^\circ$. H. W.

Constituents of "senso." X. Isomeric anhydrogamabufotalins. H. KONDO and S. OHNO

(J. Pharm. Soc. Japan, 1939, **59**, 186—189; cf. A., 1939, II, 438).—The action of 5% H_2SO_4 -EtOH on gamabufotalin (I) gives a compound, $\text{C}_{24}\text{H}_{32}\text{O}_4 \cdot \text{H}_2\text{O}$, m.p. 125—127° (decomp.), which passes at 110°/high vac. into anhydrogamabufotalin (II) of m.p. 204°.



Dry HCl in EtOH-Et₂O converts (I) into anhydrogamabufotalin (III) of m.p. 260°, with small amounts of a chlorinated material. Cone. H_2SO_4 and (I) at room temp. give a non-cryst. product from which (II) and (III) can be extracted. (II) yields a non-cryst. acetate but a cryst. (mono-*p*-nitrobenzoate. The amorphous acetate and *p*-nitrobenzoate of (III)



are diacyl compounds. Isomerisation of (II) to (III) is therefore accompanied by the formation of a new sec. OH. The spectra of (II) and (III) show a max. absorption at 290—300 μ , so that the unsaturated δ -lactone has remained intact. Catalytic hydrogenation of (II) and (III) results in the absorption of $\sim 4 \text{ H}_2$ with production of the corresponding acids, $\text{C}_{24}\text{H}_{40}\text{O}_4$, m.p. 210—212° [from (II)] and m.p. 199—201° [from (III)], which are isomeric with dihydroxy-cholanic acid. The neutral compounds which are obtained with the acids and their acyl derivatives are non-cryst. but the *p*-nitrobenzoate derived from (II) is a diacyl and that from (III) is a monoacyl derivative. It is very probable that (II) has an oxide ring between a *tert.* and a *sec.* OH of the sterol nucleus and that during conversion into (III) with opening of the oxide ring the elimination of the *tert.* OH takes place as 1 H_2O . (II) and its hydrogenation product do not contain a double linking in the sterol nucleus and can give only monoacyl derivatives. The position and configuration of the OH on the sterol nucleus is not clearly defined. Since cinobufagin and bufotalin acetate after hydrolysis give only monoacyl derivatives, the products of their hydrolysis probably contain an oxide ring.

H. W.

Configurations of the $\text{C}_{(2)}$ and $\text{C}_{(3)}$ hydroxyl groups in gitogenin and digitogenin. K. GANAPATHI (Current Sci., 1940, **9**, 18—19; cf. A., 1940, II, 14; Noller, A., 1939, II, 546; Marker *et al.*, *ibid.*, 548).—Assuming the pptn. with digitonin to have the same significance for the steroid sapogenins as for the sterols (Noller), it is to be concluded that OH at $\text{C}_{(3)}$ in gitogenin (I) and digitonin (II) is of the β -configuration, *i.e.*, *cis* to Me at $\text{C}_{(10)}$. By the other OH at $\text{C}_{(2)}$ occupying the two possible positions *cis* and *trans* with reference to Me at $\text{C}_{(10)}$ two forms are possible in which the two OH (which are *cis* to each other in both forms) are unsymmetrical or symmetrical respectively about the plane of the C atoms 2, 3, 5, and 9. (These two forms correspond with

those of B and A respectively of 2:3-dihydroxy-*trans*-decahydronaphthalene.) By analogy with the above from B, the sapogenins would be expected to isomerise to the *trans*-form on treatment with acid if these OH possessed the unsymmetrical configuration. Since this has not been observed it is concluded that in (I) and (II) the OH at $\text{C}_{(3)}$ and $\text{C}_{(2)}$ (which are in *cis* positions to each other) are *cis* and *trans* respectively with respect to Me at $\text{C}_{(10)}$.

H. W.

Saponins and sterols. XIV. Anhydro-compounds of ursolic acid. K. FUJII and S. OOSUMI (J. Pharm. Soc. Japan, 1939, **59**, 237—239; cf. A., 1940, II, 99).—The "chloride" obtained from ursolic acid by PCl_5 is reduced by Zn dust in AcOH to a neutral substance. Me ursolate (I) and PCl_5 give a non-cryst. product, reduced by Zn dust-AcOH to the anhydro-ester, Me ursylenate, $\text{C}_{31}\text{H}_{48}\text{O}_2$, m.p. 163—165°, isomerised by Zn-Hg-HCl-AcOH to Me isoursylenate, m.p. 164—167°, and hydrolysed by NaOH-KOH-EtOH- H_2O (1:2:16:4) at 145—150° to ursylenic acid (II), m.p. 266—268° (unchanged by Zn-Hg-HCl-AcOH). Me oleanolate, (I), and the Me ester of sanguisorbigenin are similarly hydrolysed. H_2 -Pd-C reduces (II) to ursenic acid, $\text{C}_{30}\text{H}_{48}\text{O}_2$, m.p. 203—205° (Me ester, m.p. 138—140°). R. S. C.

Pachymic acid, a new constituent of "Bukuryo" (*Poria cocos*, Wolf.). I. S. NAKANISHI, M. YAMAMOTO, and H. IKEDA (J. Pharm. Soc. Japan, 1939, **59**, 273—276).—An ether extract of "Bukuryo" (*P. cocos* = *Pachyma Hoelen*, Rumph; a Chino-Japanese drug) gives pachymic acid, $\text{C}_{30}\text{H}_{44}\text{O}_5$, m.p. 300° (acetate, m.p. 225°; Me ester, m.p. 175°, and its acetate, m.p. 155°), monobasic and containing one lactone group, one double linking, and one OH.

A. T. P.

Hydroxylation of furan ring. Y. OBATA (J. Agric. Chem. Soc. Japan, 1940, **16**, 187—191).—Pyromucic acid tetrabromide with moist Ag_2O gives an acidic substance which easily decomposes into $\text{H}_2\text{C}_2\text{O}_4$ and a resin. Oxidation with KMnO_4 gives 2 mols. of $\text{H}_2\text{C}_2\text{O}_4$. Since oxidation with $\text{Pb}(\text{OAc})_4$ yields $\text{CHO} \cdot \text{CO}_2\text{H}$ it is concluded the substance contains the grouping $\text{CO}_2\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH})$.

J. N. A.

Reduction of a mixture of benzaldehyde and crotonaldehyde. Z. C. GLACET (Compt. rend., 1940, **210**, 479—480).—PhCHO and $\text{CHMe} \cdot \text{CH} \cdot \text{CHO}$ with Mg-AcOH give 5-hydroxy-2-phenyl-3-methyl- or 3-hydroxy-2-phenyl-5-methyl-2:3:4:5-tetrahydrofuran (I), b.p. 105—108°/0.5 mm. [Ac derivative (II), b.p. 112°/0.6 mm.]. (II) when heated at 150—175°/40 mm. pressure, or (I) when dehydrated with CuSO_4 (poor yield), gives 2-phenyl-3-methyl-2:3-dihydro- or 2-phenyl-5-methyl-4:5-dihydro-furan, b.p. 99—100°/13 mm. J. L. D.

Bromination of pyromucic acid. Y. OBATA (J. Agric. Chem. Soc. Japan, 1940, **16**, 184—186).—Pyromucic acid with Br vapour or with Br in Et₂O at 0° gives only δ -bromopyromucic acid; with dry Br below 0° it yields pyromucic acid tetrabromide, m.p. 159.5—160° (decomp.). J. N. A.

Reaction of bromine with furfuraldehyde and related compounds. E. E. HUGHES and S. F.

ACREE (J. Res. Nat. Bur. Stand., 1940, **24**, 175—180).—The mechanism of the reaction of Br in aq. solution with equimols. of furfuraldehyde (I), methylfurfuraldehyde (II), or furoic acid (III) is discussed. With (I) and (III) there is no decrease in acidity at any time during the reaction, but with (II), >2 equivs. of acid (methylfuroic or other acid) are formed per mol. of Br consumed. Equimols. of (I) and Br in H₂O at 0° give a compound which affords a (?) bisphenylhydrazone, m.p. 155°, of a hydroxy- or keto-dihydrofurfuraldehyde; the reaction consists in addition of 2 OH to a positive double linking and formation of 2 equivs. of HBr. With the addition of minor side reactions, (II) and (III) behave similarly to (I). A. T. P.

2-Furfurylpropylamine and di-2-furfuryl tert. amines. J. E. ZANETTI and J. T. BASHOUR (J. Amer. Chem. Soc., 1940, **62**, 742—743).—Addition of the appropriate furfurylalkylamine to 2-furfuryl bromide in Et₂O with some cooling gives ~80% of *di-2-furfuryl-methyl-*, b.p. 100—102°/5 mm. (153—154°), *-ethyl-*, b.p. 109—110°/5 mm. (149—151°), *-n-propyl-*, b.p. 115—117°/5 mm. (147—148°), *-n-butyl-*, b.p. 126—128°/5 mm. (105—106°), and *-n-amyl-*, b.p. 137—139°/5 mm. (103—105°), *-amine* and *NN-di-2-furfurylaniline*, m.p. 31—32°, b.p. 163—167°/5 mm. (137—141°), figures in parentheses being m.p. of the hydrochlorides. *2-Furfuryl-n-propylamine*, b.p. 80—81°/20 mm. (*hydrochloride*, m.p. 138—140°), is prepared (method: A., 1940, II, 19). R. S. C.

Lichen pigments of the pulvic acid series. VI. Synthesis of atromentic acid. M. ASANO and S. HUIZWARA (J. Pharm. Soc. Japan, 1939, **59**, 284—286; cf. A., 1935, 1238).—*pp'*-Dimethoxydiphenylketipinodinitrile (I) and HI (*d* 1.7) in AcOH give atromentic acid (II), converted by Ac₂O—H₂SO₄ into the Ac₂ derivative, m.p. 270—271°, of the lactone (cf. Kōgl *et al.*, A., 1928, 1250, 1251). (I) and 60% H₂SO₄—AcOH give *pp'*-dimethoxypulvic anhydride (III), m.p. 266—268°, and some corresponding acid, m.p. 212°; the latter is also obtained from the Et ester, m.p. 160° [from (I)—H₂SO₄—EtOH]. (III) and HI—AcOH give (II). A. T. P.

Lichen pigments of the pulvic acid series. VII. Reduction of vulpic acid. M. ASANO and Y. ARATA (J. Pharm. Soc. Japan, 1939, **59**, 286—290; cf. A., 1935, 1238).—Vulpic acid (I) and Na—Hg (CO₂) afford Me dihydrocornicularate, m.p. 67°, and *dihydro-* (II), m.p. 194—196° (*benzoate*, m.p. 138—139°), and *isodihydro-vulpic acid* (III), m.p. 123—127°. Boiling aq. Ba(OH)₂ and (II) or (III) give *dihdropulvic acid* (IV), m.p. 208—210°, converted by Ac₂O into *cornicularlactone carboxylic acid*, m.p. 218—219° [*Me ester* (V), m.p. 170—172°]. Distillation of (IV) at 210°/6 mm. gives *cornicularlactone* (VI), m.p. 136—136.5°. (V) and Na—Hg (CO₂) give a H₂-derivative [boiling aq. Ba(OH)₂ gives phenylsuccinic acid] and *Me αδ-diphenyladipate*, m.p. 139—142° (*acid*, m.p. 247—250°). With Na—Hg (CO₂) (VI) gives αδ-diphenylvalerolactone and with Zn—AcOH dihydro-cornicularlactone and -cornicularic acid. Vulpic acid absorbs H₂ (Pd—C) slowly to give (II). Pulvinone and Na—Hg (CO₂) give dihydropulvinone,

m.p. 215—219° (*benzoate*, m.p. 140—141°) (cf. Claisen *et al.*, A., 1895, i, 373). A. T. P.

α-Tocopherolquinone. P. KARRER and A. GEIGER (Helv. Chim. Acta, 1940, **23**, 455—459).—Homogeneous α-tocopherolquinone (I) is readily obtained by oxidation of *dl*-α-tocopherol with AuCl₃ whereas repeated treatment is necessary if FeCl₃ is used. The use of AgNO₃ leads to a non-homogeneous product. (I) in .25-mg. doses is physiologically inactive. H. W.

Nitration of β-3 : 4 : 5-trimethylphenylisovaleric acid and its methyl ester. I. Formation of 5-nitro-4 : 4 : 6 : 7 : 8-pentamethyl-dihydrocoumarin. L. I. SMITH and W. W. PRICHARD (J. Amer. Chem. Soc., 1940, **62**, 780—784).—3 : 4 : 5-C₆H₂Me₃·CMe₂·CH₂·CO₂Me and KNO₃—H₂SO₄—CHCl₃ at -15° to 5° give 53% of 5-nitro-4 : 4 : 6 : 7 : 8-pentamethyldihydrocoumarin (I), m.p. 152.5—153° [also obtained in 20% yield from the corresponding acid by HNO₃ (*d* 1.6)], and 45% of a substance, C₁₅H₂₀O₆N₂, m.p. 125—125.5°. (I) yields (granulated Zn—AcOH—H₂O) the 5-NH₂-derivative (II), m.p. 125—125.5°, which, pptd. from dil. NaOH by acid, gives 5-hydroxy-4 : 4 : 6 : 7 : 8-pentamethyldihydrocarbo-styryl, m.p. 193—194° (does not couple; *acetate*, m.p. 207—208°). By diazo-reactions (II) gives 5-iodo-, m.p. 131.5—132.5° (loses I to boiling 20% KOH), and 5-hydroxy-4 : 4 : 6 : 7 : 8-pentamethyldihydrocoumarin, m.p. 207—208° (*Me ether*, m.p. 132—132.5°, resists further methylation, benzoylation, and fission by 20% KOH). R. S. C.

Pyrone series. Attempted oxidation of chromanones with selenium dioxide. I. D. CHAKRAVARTI and J. DUTTA (J. Indian Chem. Soc., 1939, **16**, 639—644).—Condensation of the appropriate phenol with Cl[CH₂]₂·CO₂H in KOH gives the phenoxypropionic acid, cyclised in C₆H₆ with P₂O₅. The following are described: β-(*p*-chloro-, m.p. 138—139°, β-(*o*-chloro-, m.p. 108—109°, β-(*p*-nitro-, m.p. 118—119°, β-(*o*-nitro-, m.p. 121—122°, β-(*o*-methyl-, m.p. 94—95°, and β-(*p*-methyl-phenoxy)-, m.p. 146°, and β-(2-naphthoxy-, m.p. 144—145°, and β-(1-naphthoxy-propionic acid, m.p. 147—148°; 6-chloro-, m.p. 106° (3-veratrylidene derivative, m.p. 151—152°), 8-chloro-, m.p. 65° (3-veratrylidene derivative, m.p. 110—111°), 6-nitro-, m.p. 176—177° (3-veratrylidene derivative, m.p. 190—191°), 8-nitro-, m.p. 126—127° (3-veratrylidene derivative, m.p. 179—180°), β-naphtha-, b.p. 185—187°/9 mm. [*semicarbazone*, m.p. 227° (decomp.)], α-naphtha-, m.p. 104° (3-veratrylidene derivative, m.p. 169—170°, 8-methyl-, 125—130°/9 mm. [*semicarbazone*, m.p. 230—231° (decomp.)], and 6-methyl-chromanone, b.p. 118—126°/6 mm. (3-veratrylidene derivative, m.p. 131—132°). The chromanones are not oxidised with SeO₂ to chromones, although the flavanones and chalkones are oxidised with SeO₂ to the flavones. 5-Chloro-2-hydroxy-3' : 4'-dimethoxychalkone, m.p. 174°, is oxidised to 6-chloro-3' : 4'-dimethoxyflavone, m.p. 194°, and the 3-chloro-chalkone, m.p. 163—164°, similarly affords the 8-chloro-flavone, m.p. 110° (decomp.). 3-Nitro-2-hydroxy-3' : 4'-dimethoxy-5-methylchalkone, m.p. 175°, yields 8-nitro-3' : 4'-dimethoxy-6-methyl-flavone, m.p. 244—245° (decomp.). F. R. S.

Syntheses of 5:6- and 5:8-dihydroxyflavone and constitution of primetin. Z. HORII (J. Pharm. Soc. Japan, 1939, 59, 209—214).—Primetin is shown to be 5:8-dihydroxyflavone (I). 1:2:6-C₆H₃Ac(OH)₂ is converted by CH₃N₂ in Et₂O into 2-hydroxy-6-methoxyacetophenone, b.p. 141°/16.5 mm., m.p. 57—58°, which with alkaline K₂S₂O₈ and then HCl at 100° gives 2:5-dihydroxy-6-methoxyacetophenone (II), b.p. 155—160°/5.5 mm., m.p. 91.5—92.5° (Ac₂, m.p. 66.5—67.5°, and Bz₂, m.p. 153.5—154.5°, derivatives). Bz₂O, NaOBz, and (II) at 175—185° afford 6-hydroxy-5-methoxyflavone, m.p. 183.5—185° (Ac derivative, m.p. 136—137°), which is demethylated (AlCl₃ in PhNO₂ at 100° or by 20% HCl or HI) to 5:6-dihydroxyflavone (III), m.p. 189—191° (Ac₂ derivative, m.p. 165—166.5°). Alternatively (II) is completely methylated to 2:5:6-trimethoxyacetophenone (IV), b.p. 163.5°/11 mm., which is condensed with EtOBz and Na and then hydrolysed by HI to (III). (IV) is partly demethylated by NH₂Ph, HI and NH₂Ph at 120—130° to 6-hydroxy-2:5-dimethoxyacetophenone, b.p. 136°/2 mm., m.p. 61.5—62.5°, transformed by BzCl and C₅H₅N into the benzoate, m.p. 120—121°, which with NaNH₂ in dry PhMe at 100° gives 6-hydroxy-2:5-dimethoxy- ω -benzoylacetophenone, m.p. 167—168°. This with NaOAc and glacial AcOH, or conc. H₂SO₄ at 100°, gives 5:8-dimethoxyflavone, m.p. 145.5—146.5°, which is unaffected by boiling 20% HCl but is partly demethylated by AlCl₃ in boiling CS₂ to 5-hydroxy-8-methoxyflavone, m.p. 210° (acetate, m.p. 176°), which does not depress the m.p. of the Me ether of (I). H. W.

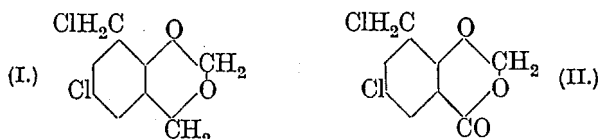
Flavones, flavanones, and flavonols derived from hydroxyquinol. G. BARGELLINI and G. B. MARINI-BETTOLO (Gazzetta, 1940, 70, 170—178).—1:2:4:5-C₆H₂Ac(OMe)₃ with boiling conc. HCl gives 2:1:4:5-OH·C₆H₂Ac(OMe)₂ (I). With PhCHO in EtOH-KOH, followed by CO₂, (I) gives 2-hydroxy-4:5-dimethoxychalcone (II), m.p. 98°, and, especially when the amount of KOH and the temp. are increased, 6:7-dimethoxyflavanone (III), m.p. 170—171°, also obtained by heating (II) in dil. HCl-EtOH. When heated with dil. KOH and treated with CO₂, (II) gives 6:7-dimethoxyflavone. With H₂O₂ in EtOH-KOH, (II) or (III) yields 6:7-dimethoxyflavanol, m.p. 198°, which with HI gives a red product. With anisaldehyde, (I) similarly gives 2-hydroxy-4:5:4'-trimethoxychalcone (cf. Bargellini *et al.*, A., 1911, i, 855) and 6:7:4'-trimethoxyflavanone, m.p. 154°. SeO₂ in C₅H₁₁·OH oxidises (IV) to 6:7:4'-trimethoxyflavone, whilst H₂O₂ yields 6:7:4'-trimethoxyflavanol, m.p. 230°, with (in presence of excess of H₂O₂) 2:4:5:1-OH·C₆H₂(OMe)₂·CO₂H. With veratraldehyde, (I) gives, by similar methods, 2-hydroxy-4:5:3':4'-tetramethoxychalcone, m.p. 152°, and 6:7:3':4'-tetramethoxyflavanone, m.p. 161°, flavone, m.p. 219°, and flavanol, m.p. 228°, and with piperonal, 2-hydroxy-4:5-dimethoxy-3':4'-methylenedioxychalcone, m.p. 189°, and 6:7-dimethoxy-3':4'-methylenedioxyflavanone, m.p. 176°, flavone, m.p. 250°, and flavanol, m.p. 258°. E. W. W.

Synthesis of derivatives of diphenylene dioxide. XV. α -Keto- (or -hydroxy-) β -(or - γ -)morpholylalkyldiphenylene dioxides. M.

TOMITA (J. Pharm. Soc. Japan, 1939, 59, 205—206; cf. A., 1939, II, 442).—Treatment of 2:6-di- β -halogeno- α -ketoethyldiphenylene dioxide with morpholine gives 2:6-di- α -keto- β -morpholinoethyldiphenylene dioxide, m.p. 195° (hydrochloride, m.p. >300°), reduced (Na-Hg or H₂-PtO₂) to 2:6-di- α -hydroxy- β -morpholinoethyldiphenylene dioxide, m.p. 202°. The following are obtained analogously: 3:7-dimethyl-2:6-di- α -keto-, m.p. 171° (hydrochloride, m.p. >300°), and - α -hydroxy-, m.p. 242°, - β -morpholinoethyldiphenylene dioxide; 2:6-di- α -keto-, m.p. 176° (hydrochloride, m.p. >280°), and - α -hydroxy-, m.p. 199°, - γ -morpholinopropyldiphenylene dioxide; 2:6-di- α -keto-, m.p. 184° (hydrochloride, m.p. >280°), and - α -hydroxy-, m.p. 220—232°, - β -morpholinopropyldiphenylene dioxide. The properties of these compounds are similar to those of the piperidino-derivatives (*loc. cit.*). H. W.

Photolysis of rhodamine. E. BAUR (Atti X Congr. Internaz. Chim., 1938, 4, 417).—Anaërobic irradiation of rhodamine (I)-3B, -3G, or -6G adsorbed on colophony (II) sol affords CH₂O. The non-Et-esterified forms of (I) [e.g., (I)G] do not yield CH₂O. The effect is independent of the nature of the alkyl group. (I)G gives CH₂O when (II) is replaced by MeOH, PrOH, and other alcohols, probably owing to ester formation during irradiation. F. O. H.

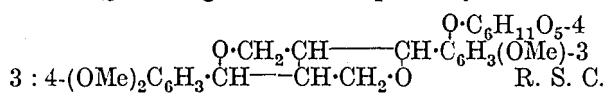
Proof of structure of 6-chloro-8-chloromethyl-1:3-benzdioxan by oxidation. C. A. BUEHLER, B. C. BASS, R. B. DARLING, and M. E. LUBS (J. Amer. Chem. Soc., 1940, 62, 890—894).—Passage of HCl into *p*-C₆H₄Cl-OH in 40% CH₂O-conc. HCl-H₂SO₄ at 40° gives 6-chloro-8-chloromethyl-1:3-benzdioxan (I), m.p. 103°, which with CrO₃-AcOH gives



6-chloro-8-chloromethyl-1:3-benzdioxan-4-one (II), m.p. 181—182°, hydrolysed by NaOH to 5-chloro-2-hydroxy-3-hydroxymethylbenzoic acid (III), m.p. 166.5—167° (purple FeCl₃ colour). KMnO₄ oxidises (I) in boiling AcOH-H₂O to 6-chloro-8-aldehydo-1:3-benzdioxan-4-one (IV), m.p. indefinite (reduces Tollens' reagent), 5-chloro-2-hydroxy-3-aldehydobenzoic acid (V), +H₂O, m.p. 217—221°, 5-chloro-2-hydroxy-isophthalic acid (VI), +H₂O, m.p. 238—240° (red FeCl₃ colour; Et₂ ester, m.p. 50—51°), and small amounts of (II) and 6-chloro-8-aldehydo-1:3-benzdioxan (VII), m.p. 138—138.5° (phenylhydrazones, m.p. 152.5—155°). (V) and (VI) are formed by oxidation of (IV), which is formed by way of (II) and (VII). The dioxanone ring of (IV) is easily ruptured: titration with alkali gives (V), NH₂OH, HCl and 10% NaOH give the oxime, m.p. 199.5—200.5°, of (V), and H₂-Raney Ni in EtOAc at 2.5 atm. gives (III). α -OH·C₆H₄·CO₂H, CHCl₃, and aq. NaOH at 80° give 3:2:1-CHO·C₆H₃(OH)·CO₂H, converted by Cl₂ in AcOH into an anhyd. form, m.p. 226°, of (V), which with KMnO₄ in AcOH-H₂O gives an anhyd. form, m.p. 245—246°, of (VI). R. S. C.

Forsythian as isomeride of phillyrin (philyr-oxide). Its constitution. T. KAKU, H. RI, and

N. HARA (J. Pharm. Soc. Japan, 1939, **59**, 248—255).—Forsythine exists in α -, m.p. 154—155°, and β -forms, m.p. 184—185°, $[\alpha]_D$ (both) +64.6° (63.9°) in C_5H_5N , +48.4° (48.5°) in EtOH, of which the former is identical with phillyrin. CH_2N_2 or Me_2SO_4 converts forsythegenol into epipinoresinol Me_2 ether $[(NO_2)_2$ -derivatives, (i) m.p. 230°, $[\alpha]_D$ +119.7°, (ii) forms, m.p. 161—162° (unstable) and 180°, $[\alpha]_D$ +147.4°]. The glucosides are probably



Derivatives of 4-phenylpentamethylene oxide and sulphide.—See B., 1940, 346.

Oxidation of thiophen-sulphur by calcium hypochlorite solutions.—See A., 1940, I, 268.

Thiophen series. LI. Atophan-like derivatives of dithienyl and diphenyl. W. STEINKOPF and H. J. VON PETERSDORFF (Annalen, 1940, **543**, 119—128; cf. A., 1939, II, 443).—Isatin (I), p - C_6H_4 Ph·COMe, and 28% KOH with a little EtOH at 110° (bath) give 2- p -diphenyllylquinoline-4-carboxylic acid, m.p. 289—290°, decarboxylated (soda-lime) to 2- p -diphenyllylquinoline, m.p. 175—177°. (C_6H_4 ·COMe- p)₂ and (I) similarly give 4:4'-di-(4''-carboxy-2''-quinolyl)diphenyl, m.p. >320°, whence 4:4'-di-2''-quinolylidiphenyl, m.p. 314—315°. 2:2'-Dithienyl, AcCl, and $TiCl_4$ in C_6H_6 at 100° (bath) afford 5-acetyl-, m.p. 114.5—115.5°, and 5:5'-diacetyl-2:2'-dithienyl, m.p. 231—232°, converted (as above) into 5-mono-, m.p. 237—238°, and 5:5'-di-(4''-carboxy-2''-quinolyl)-2:2'-dithienyl, amorphous (Me_2 ester, m.p. 271—273°), respectively, whence 5-mono-, m.p. 142—143°, and 5:5'-di-(2''-quinolyl)-2:2'-dithienyl, m.p. 243—244°, respectively. 3:3'-Diacetyl-5:5'-dimethyl-2:2'-dithienyl, m.p. 109—111° (from the Me_2 derivative, AcCl, and $AlCl_3$ in CS_2), gives 3:3'-di-(4''-carboxy-2''-quinolyl)-5:5'-dimethyl-2:2'-dithienyl, hygroscopic, m.p. 209° (decomp.), +AcOH, m.p. 222—224°. 2:5:2':5'-Tetramethyl-3:3'-dithienyl, AcCl, and $TiCl_4$ in C_6H_6 afford the 4:4'- Ac_2 derivative, m.p. 90—91°; 2-phenylthiophen similarly yields 5-phenyl-2-acetothienone, m.p. 115—118°, whence 5-phenyl-2,4'-carboxy-2'-quinolylthiophen, m.p. 230—231°. Acetylthiophthen and (I) give 2(or 3)-4'-carboxy-2'-quinolylthiophthen, m.p. 260—262° (blackening), whence 2(or 3)-2'-quinolylthiophthen, m.p. 214—215°. Many of the compounds show luminescence in Hg light. H. B.

Thiophen series. LII. Derivatives of 3-bromo- and 2:3-dibromo-thiophen. W. STEINKOPF and, in part, H. J. VON PETERSDORFF (Annalen, 1940, **543**, 128—132).—3-Bromothiophen (I), b.p. 154—160° [from 2:3-dibromothiophen (II), EtBr, and Mg in Et_2O and subsequent hydrolysis], with $Hg(OAc)_2$ in AcOH at 50—55° and the b.p. gives the 2:5-di- and 2:4:5-tri-acetoxymercuri-derivatives, respectively, converted (usual method) into 3-bromo-2:5-di-iodo- (III), m.p. 55—56°, and -2:4:5-tri-iodo-thiophen, m.p. 156—157°, respectively. An excess of Br rapidly converts (III) into tetrabromothiophen. 3-Bromothiophen-2-sulphonic acid (amide, m.p. 163—164°) is formed from (I) and cold $ClSO_3H$.

2:3-Dibromo-5-iodothiophen, m.p. 58—58.5° [from (II), HgO , and I in C_6H_6], with Cu-bronze at 240° affords 4:5:4':5'-tetrabromo-2:2'-dithienyl, m.p. 181° (with Br gives hexabromo-2:2'-dithienyl). The di-, tri-, and tetra-chloro-2:2'-dithienyl of Eberhard *et al.* (A., 1894, i, 117; 1896, i, 16) are the 5:5'-, 3:5:5'-, and 3:5:3':5'-derivatives, respectively. H. B.

Some reactions of Δ^{β} - γ -lactones. E. WALTON (J.C.S., 1940, 438—442).—The statement of Lukeš *et al.* (A., 1929, 824) that lactones of type $\begin{array}{c} CH \cdot CR' \\ CH_2 \cdot CO > O \end{array}$

(A) with amines give not pyrrolidones of type $\begin{array}{c} CH_2 \cdot CH_2 \\ CO-NR \end{array} > R' \cdot OH$, but open-chain amides,

$NHR \cdot CO \cdot [CH_2]_2 \cdot COR'$, is incorrect. Their "læval-anilide" obtained from Δ^{β} -angelicalactone (I) (A; $R' = Me$) and NH_2Ph at 180°, is identical with 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone (II) (*loc. cit.*), which with $Br-H_2O$ gives the corresponding 1- p -bromophenyl compound, m.p. 159—161° (decomp.), also obtained from (I) and p - $C_6H_4Br \cdot NH_2$ (III). Succinyl with $MgMeI$ in C_6H_6 also gives (II) (mixed m.p.). γ -Phenyl- Δ^{β} -crotonolactone (IV) (A; $R' = Ph$) with conc. aq. NH_3 gives 2-hydroxy-2-phenyl-5-pyrrolidone (V), and with 33% aq. NH_2Me , NH_2Et , and NH_2Pr^a gives 2-hydroxy-2-phenyl-1-methyl- (VI), m.p. 130—135° (decomp.) [also obtained from succinomethylimide (VII) (cf. Lukeš *et al.*, A., 1928, 897)], -1-ethyl-, m.p. 85—87°, and -1- n -propyl-5-pyrrolidone, m.p. 85—86°. These products (in the formation of which there are colour changes from green through blue, violet, and red, to yellow) are all amphoteric, dissolving in 6N-HCl and in 2N-NaOH. In the latter, (V) is decomposed, but (VI) may be refluxed unchanged for 5 min., and its homologues are also stable; the compounds are, however, hydrolysed by aq. HCl or $EtOH-HCl$ to $CH_2Bz \cdot CH_2 \cdot CO_2H$ and NH_2R . With boiling NH_2Ph , (IV) gives 2-hydroxy-1:2-diphenyl-5-pyrrolidone, m.p. 148—149°, which with $Br-H_2O$ forms 2-hydroxy-2-phenyl-1- p -bromophenyl-5-pyrrolidone, m.p. 166°, also obtained from (III) and (IV). p - $C_6H_4Me \cdot CO \cdot [CH_2]_2 \cdot CO_2H$ and Ac_2O at 100° give γ - p -tolyl- Δ^{β} -crotonolactone (VIII), m.p. 111°, which with conc. aq. NH_3 at 100° gives 2-hydroxy-2- p -tolyl-5-pyrrolidone, m.p. 165—167° (decomp.), previously regarded as an open-chain amide. With 33% aq. NH_2Me , (VIII) gives 2-hydroxy-2- p -tolyl-1-methyl-5-pyrrolidone, m.p. (+0.5H₂O) 92—93°, (anhyd.) 132—140° (decomp.), also obtained from (VII) and p - $C_6H_4Me \cdot MgBr$ in C_6H_6 . p - $C_6H_4Br \cdot CO \cdot [CH_2]_2 \cdot CO_2H$ with Ac_2O at 100° gives γ - p -bromophenyl- Δ^{β} -crotonolactone, m.p. (impure) 115—130° (decomp.), which with warm aq. NH_3 and with 33% aq. NH_2Me gives respectively 2-hydroxy-2- p -bromophenyl-5-pyrrolidone, m.p. 169—171° (decomp.), and -1-methyl-5-pyrrolidone, m.p. 145—148° (decomp.) [also obtained from (VII) and p - $C_6H_4Br \cdot MgBr$]. Similarly γ - p -anisyl- Δ^{β} -crotonolactone, m.p. 110—111° (obtained as before) gives 2-hydroxy-2- p -anisyl-5-pyrrolidone, m.p. 133—135°, and -1-methyl-5-pyrrolidone, m.p. 88—92° [not obtained from (VII)]. The above pyrrolidones are hydrolysed by HCl as before. Attempts to confirm the presence of OH in (VI) were unsuccessful, there being no reaction with Me_2SO_4 ,

Ac₂O, or PhNCO, and AcCl causing elimination of H₂O to give an unsaturated product. E. W. W.

Derivatives of substituted succinic acids. IV.

Action of alkaline sodium hypobromite on some α -alkyl- α' -arylsuccinamides. J. A. McRAE and (Miss) N. A. McGINNIS (Canad. J. Res., 1940, 18, B, 90—95).—The NH₄ salt of phenylmethylsuccinic acid when heated at 180° gives α -phenyl- α' -methylsuccinimide, m.p. 109°, which with NH₃-EtOH affords the -amide, m.p. 224—225°. This amide with NaOBr is converted into 6-phenyl-5-methylhydriouracil, m.p. 192—195° (lit. 185°), not identical with the corresponding 5-phenyl-6-methyl compound (I), m.p. 224°. β -Amino- α -phenylbutyric acid, m.p. 248°, prepared from Me α -phenylcrotonate and NH₂OH, with KCNO yields β -ureido- α -phenylbutyric acid, which when heated is converted into (I). β -Cyano- β -phenyl- α -n-hexylpropionic acid, m.p. 166°, obtained from heptylidene-phenylacetonitrile and KCN, is difficult to hydrolyse and the succinic acid is directly converted into α -phenyl- α' -n-hexylsuccinimide, m.p. 52°, by heating the NH₄ salt, and thence with NH₃-EtOH into the -amide, m.p. 233° (decomp.). This amide with NaOBr gives β -phenylureido- α -n-hexylpropionic acid, m.p. 144—145° (decomp.). α -Phenyl- α' -benzylsuccinimide, m.p. 131°, is converted (NH₃-EtOH) with difficulty into the -amide, m.p. 216°, which with NaOBr has given a substance, m.p. 219°, which could not be characterised. F. R. S.

Identification of organic compounds. II.

Piperidyl derivatives of aromatic halogenonitro-compounds. (Miss) M. K. SEIKEL (J. Amer. Chem. Soc., 1940, 62, 750—756; cf. A., 1940, II, 160).—Conditions are defined for conversion of aromatic halogenonitro-compounds into piperidino-derivatives. The following compounds are described, the piperidino-group being inserted, unless otherwise stated, by replacement of halogen. 1-Chloro-2:4-dinitro-5-, m.p. 114—114.5° (lit., 117—118°, 119°), 1:3-dibromo-2:4-dinitro-5-, m.p. 129—129.5°, 1-chloro-4-nitro-3-[from 1:3:4-C₆H₃Cl(NO₂)₂ (I) or -C₆H₃Cl₂NO₂ (II), 1:2:3:5-C₆H₃Cl(NO₂)₃ or -C₆H₃Cl₂(NO₂)₂], m.p. 125.5°, 1:3-dichloro-5-nitro-(?) 2-[from 1:3:2:5-C₆H₃Cl₂(NO₂)₂], m.p. 86.5—87.5°, 1:3-dichloro-5-nitro-4-, m.p. 57—58°, 1-chloro-2:3-dinitro-4-[from 1:4:2:3-C₆H₃Cl₂(NO₂)₂], m.p. 91—92°, 1-chloro-2:5-dinitro-4-, m.p. 71.5—72.5°, 1:2-dichloro-4-nitro-3-, m.p. 73—74°, 1:3-dichloro-4-nitro-5-, m.p. 41—42°, 1:2-dichloro-3:5-dinitro-6-, m.p. 95—96°, and 1:3-dibromo-4-nitro-5-, m.p. 70—71°, -1'-piperidino-benzene; 1-nitro-2:5-[from (I) or (II)], m.p. 77.5—78.5°, 1-chloro-3-nitro-4:6-[from 1:2:4:5-C₆H₃Cl₂(NO₂)₂ or -C₆H₃Cl₂NO₂], m.p. 103.5—104° and (+ piperidine) ~125°, 1:2-dinitro-3:5-, m.p. 173—173.5°, 1:2-dinitro-3:6-, m.p. 167—167.5°, 1-chloro-3-nitro-2:6-, m.p. 93.5—94°, 1-chloro-4-nitro-3:5-, m.p. 88.5—89.5°, 1-chloro-3:5-dinitro-2:6-, m.p. 188.5—189°, 1-chloro-3:5-dinitro-2:4-, forms, m.p. 142.5—143° and (stable) 146.5—147.5°, 1-chloro-2:6-dinitro-3:5-, m.p. 190°, 1-bromo-4-nitro-3:5-, m.p. 87.5—88°, and 1-bromo-2:4-dinitro-3:5-, m.p. 224—225°, -dipiperidinobenzene; 1-o-, m.p. 38—39° (hydrochloride, m.p. 210.5—212°), and 1-m-nitrobenzylpiperidine, m.p. 10—13° (hydrochloride, m.p.

202.5—205°). s-C₆H₃(NO₂)₃ and piperidine give an unstable additive compound, m.p. 60—62° (decomp. 110—120°). 1:3:5-C₆H₃Cl(NO₂)₂ dissolves, forming an additive compound, which is not isolated. 1:3:5-C₆H₃Cl₂NO₂, 1:2:6- and 1:4:2-C₆H₃MeClNO₂ do not react. R. S. C.

Quinuclidine derivatives.—See B., 1940, 406.

Oxalates of ammonium-pyridine platinum compounds.—See A., 1940, I, 267.

N¹N⁴-Nicotinoyl derivatives of sulphanilamide.

T. C. DANIELS and H. IWAMOTO (J. Amer. Chem. Soc., 1940, 62, 741—742).—N⁴-Nicotinoyl- (I), m.p. 257—258° (N¹-Ac derivative, m.p. 255—256°), and thence N¹N⁴-dinicotinoyl-sulphanilamide, forms, m.p. 222° and 248°, are prepared from p-NH₂-C₆H₄-SO₂-NH₂ by nicotinoyl chloride in C₅H₅N at 100° or from nicotinamide by ClSO₃H (first at <15° and then at 60°) etc. (nomenclature: A., 1938, II, 439). The pharmacological properties of (I) are promising. R. S. C.

Pyridine sulphanilamides.—See B., 1940, 405.

Phenylpyridines.—See B., 1940, 346.

Mechanism of formation of indoxyl *in vivo* from o-nitrobenzene derivatives.—See A., 1940, III, 519.

β -Indolylacetic acids.—See B., 1940, 346.

Syntheses in the indole series. I. Synthesis of indolyl-3-glyoxylic acid and of r-3-indolylglycine. J. W. BAKER (J.C.S., 1940, 458—460).—Mg indolyl iodide and CO₂MeCOCl give Me indolyl-3-glyoxylate (I), m.p. 224°, which contains a prototropic pentad system, yielding an Ac derivative, m.p. 130°, and a xenylurethane, shrinking at 167° to a clear liquid at 200°, of the enolic form. Hydrolysis (NaOH) of (I) affords the acid, m.p. 216° (decomp.), also obtained either by hydrolysis or treatment with HNO₂ of the amide, m.p. 252° (slight decomp.). Methylation (MeOH-Na-MeI) of (I) gives Me 1-methylindolyl-3-glyoxylate, m.p. 82.5°, and reduction (Al-Hg) yields Me indolyl-3-glycollate, m.p. 82.5°. Oximation of (I) affords oxime-A, m.p. 174°, and -B, m.p. 143°; the former is reduced (Al-Hg in Et₂O) to Me α -aminoindolyl-3-acetate, m.p. 118°, which is hydrolysed (NaOH) to r-3-indolylglycine, m.p. 221° (decomp.). F. R. S.

Amanita toxins. V. Constitution of phalloidine. H. WIELAND and B. WITKOP (Annalen, 1940, 543, 171—183).—Phalloidine (I), C₃₀H₃₉O₉N₇S (cf. Lynen *et al.*, A., 1938, II, 66; method of isolation modified), [α]_D +62.3° in EtOH, is hydrolysed by 30% H₂SO₄ in CO₂ at 100° (bath) to l-cysteine (isolated partly as cystine owing to subsequent autoxidation), l-alanine, l-hydroxyproline b, m.p. 241° (decomp.), [α]_D²⁰ -57.4° in H₂O (Leuchs *et al.*, A., 1920, i, 85), and l-hydroxytryptophan [α -amino- β -2-keto-2:3-dihydro-3-indolylpropionic acid] (II), m.p. 249—253° (decomp.), [α]_D²⁰ +39.2° in N-NaOH. Quant. results indicate that (I) is the hexapeptide derived by loss of 6H₂O [(I) does not contain free NH₂ or CO₂H] from 1, 2, 2, and 1 mol., respectively, of the above NH₂-

acids. Hydrolysis of (II) by short treatment with hot aq. $\text{Ba}(\text{OH})_2$ gives (probably) $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (couples with $\beta\text{-C}_{10}\text{H}_7\text{OH}$); (II) gives the Folin-Denis but not the Hopkins-Cole reaction. H. B.

Synthesis of nitrogen ring compounds. XIX. Synthesis of isoquinolines having N-hetero-ring in 1-position. S. SUGASAWA, K. SAKURAI, M. FUJISAWA, and N. SUGIMOTO (J. Pharm. Soc. Japan, 1940, 60, 39—42).—Et quinaldinate and 3:4:-(CH_2O_2) $\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NH}_2$ at $\sim 220^\circ$ give *quinaldin- β -3:4-methylenedioxyphenyl- α -methyl-ethylamide*, m.p. 125° , cyclised by POCl_3 in hot PhMe to 6:7-methylenedioxy-1-2'-quinolyl-3-methyl-3:4-dihydroisoquinoline, m.p. 143° . The corresponding dimethiodide is transformed into the methochloride, which is catalytically reduced to 6:7-methylenedioxy-1-2'-1'-methyl-1':2':3':4'-tetrahydroquinolyl-2:3-dimethyl-1:2:3:4-tetrahydroisoquinoline, characterised as the *dipicrate*, m.p. $214\text{--}215^\circ$. *Quinaldin- β -3:4-methylenedioxyphenylethylamide*, m.p. 108° , is similarly cyclised to 6:7-methylenedioxy-1-2'-quinolyl-3:4-dihydroisoquinoline, m.p. 121° , which gives only resinous products with $\text{C}_6\text{H}_5\text{Br}_2$. Catalytic reduction of 6:7-dimethoxy-1-3'-pyridyl-3:4-dihydroisoquinoline dimethochloride gives the non-cryst. 6:7-dimethoxy-1-1'-methyl-3'-piperidyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (*dipicrate*, decomp. $207\text{--}5^\circ$; *platinichloride*, decomp. 224°). β -Nicotinomoveratrylamide is catalytically reduced to 1-methyl-3-piperidylhomoveratrylamide, m.p. (crude) $\sim 95^\circ$ (*picrate*, decomp. 230°), cyclised by POCl_3 in dry PhMe to non-cryst. 6:7-dimethoxy-1-1'-methyl-3'-piperidyl-3:4-dihydroisoquinoline (*dipicrolonate*, decomp. 243°). *Chloroacet- β -methoxy- β -3:4-methylene-dioxyphenyl- α -methyl-ethylamide*, b.p. $179^\circ/3\text{--}5\text{ mm.}$, from the amine and $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in COMe_2 at 0° , is transformed by piperidine in C_6H_6 into *piperidinoacet- β -methoxy- β -3:4-methylenedioxyphenyl- α -methyl-ethylamide* (*methiodide*, decomp. $197\text{--}198^\circ$), cyclised by POCl_3 in boiling PhMe to 6:7-methylenedioxy-1-piperidinomethyl-3-methylisoquinoline, m.p. 140° (*methiodide*, decomp. $201\text{--}202^\circ$). H. W.

Hydrogenation under pressure of 6-hydroxyquinoline and its derivatives. K. MIYAKI and H. KATAOKA (J. Pharm. Soc. Japan, 1939, 59, 222—224).—6-Hydroxyquinoline is hydrogenated (20% Ni-kieselguhr in abs. EtOH) at $140^\circ/80\text{--}100\text{ atm.}$ (initial pressure) to the 1:2:3:4-tetrahydride, m.p. 160° , whereas at 180° the product is the *decahydride*, separated into a solid, m.p. 185° , and a liquid, b.p. $93\text{--}98^\circ/0\text{--}005\text{ mm.}$, portion. 6-Acetoxyquinoline in cyclohexane at 140° yields the *tetrahydride*, b.p. $130\text{--}140^\circ/0\text{--}01\text{ mm.}$ 6-Acetoxy-1-benzoyl- in abs. EtOH at 250° is converted into 6-hydroxy-1-hexahydrobenzoyl-1:2:3:4-tetrahydroquinoline, m.p. 210° , whilst 6-methoxy-1-hexahydrobenzoyl-1:2:3:4-tetrahydroquinoline, m.p. $75\text{--}76^\circ$, is obtained from the corresponding Bz derivative. H. W.

5:5-Dimethylhydantoins containing a NRR' substituent. H. R. HENZE and J. W. MAGEE (J. Amer. Chem. Soc., 1940, 62, 912—913).— $\text{COMe}\cdot\text{CH}_2\cdot\text{NRR}'$, KCN, and $(\text{NH}_4)_2\text{CO}_3$ in 50% EtOH at $55\text{--}65^\circ$ give 68—92% yields of 5-methyl-5-N-

methyl-, m.p. 190° , -ethyl-, m.p. 171° , and -benzyl-anilino-methylhydantoin, m.p. 213° , 5-methyl-5-N-benzyl-N-methyl-, m.p. 204° , -ethyl-, m.p. 165° , -n-propyl-, m.p. 157° , and -n-butyl-aminomethylhydantoin, m.p. 169° , 5-methyl-5-N-o-, m.p. 177° , and -p-methyl-benzyl-N-methylaminomethylhydantoin, m.p. 178° , and 5-methyl-5-N-cyclohexyl-N-methylaminomethylhydantoin, m.p. 199° . M.p. are corr. R. S. C.

Colour in relation to chemical constitution of the organic salts and metallic derivatives of oximinodiphenylthiohydantoin. S. DUTT and B. M. S. AGARWAL (Proc. Indian Acad. Sci., 1940, 11, A, 96—105).—Protracted action of NaNO_2 on 1:3-diphenylthiohydantoin in AcOH at room temp. gives unchanged material, an unidentified yellow substance, m.p. 245° , and *oximino-1:3-diphenylthiohydantoin* (I), m.p. 174° . (I) is bright yellow when solid or in solution in non-hydroxylic org. media but gives an intense crimson colour on addition of alkali or org. bases, thus resembling violuric acid. The change is attributed to the conversion of the oximino-ketonic into the nitroso-enolic form: $\text{CS} \begin{matrix} \text{NPh}\cdot\text{C}\cdot\text{N}\cdot\text{OH} \\ \text{NPh}\cdot\text{CO} \end{matrix} \rightarrow$

$\text{CS} \begin{matrix} \text{NPh}\cdot\text{C}\cdot\text{NO} \\ \text{NPh}\cdot\text{C}\cdot\text{OH} \end{matrix}$ (I) gives salts with NH_2Me , m.p. 120° , NHMe_2 , m.p. 148° , NMe_3 , m.p. 152° , NH_2Et , m.p. 156° , NHEt_2 , m.p. 179° , NEt_3 , m.p. 87° , NH_2Bu^t , m.p. 167° , $\text{C}_5\text{H}_5\text{N}$, m.p. 139° , piperidine, m.p. 158° , nicotine, m.p. 132° ; the *K*, m.p. 167° , *Na*, m.p. 188° , and NH_4 , m.p. 112° , salts are described.

H. W.

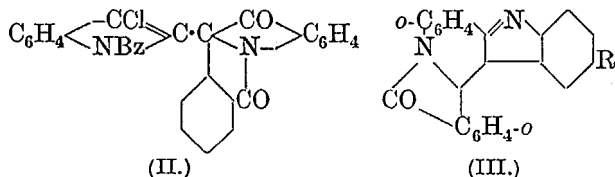
Dicyclic heterocyclic compounds with a heteroatom common to both cycles. V. PRELOG (Arh. Kemiju, 1939, 12, 97—105).—A review. R. T.

Polarisation in heterocyclic rings with aromatic character. IV. Polarisation in the glyoxaline ring. E. OCHIAI and M. SIBATA (J. Pharm. Soc. Japan, 1939, 59, 256—260; cf. A., 1939, II, 451).—2:4-Dimethylglyoxaline, PhCHO, and ZnCl_2 at $180\text{--}185^\circ$ give 2-styryl-4-methylglyoxaline, decomp. $147\text{--}148^\circ$ (*picrate*, decomp. 248°). 2-Styryl-1:1:4-trimethylglyoxalinium iodide, m.p. $248\text{--}5^\circ$ (corresponding *picrate*, m.p. $166\text{--}5^\circ$), is obtained from 1:1:2:4-tetramethylglyoxalinium iodide, hygroscopic (corresponding *picrate*, m.p. $126\text{--}5^\circ$), by PhCHO and a little piperidine at $150\text{--}165^\circ$, but 2-styryl-3:4-dimethylthiazolinium iodide, m.p. 227° (corresponding *picrate*, m.p. $163\text{--}5^\circ$), is obtained at 100° . 2:4-Diphenylglyoxaline and aq. CH_2O at $140\text{--}160^\circ$ give 2:4-diphenyl-5-hydroxymethylglyoxaline (I), decomp. 179° , and 5:5'-methylene-di-(2:4-diphenylglyoxaline) (II), $+1\text{--}5\text{H}_2\text{O}$, m.p. 256° (*dipicrate*, decomp. 212°). In boiling decahydronaphthalene (I) gives (II) and CH_2O . Hydrogenation of 5-nitro-4-methylglyoxaline in acid gives the unstable 5- NH_2 -compound (*CHPh*: derivative, m.p. 216°), but hydrogenation in presence of $\text{CH}_2(\text{COMe})_2$ gives 4:4':6'-trimethylglyoxalinol-1:5-1':2'-pyrimidine, $+ \text{H}_2\text{O}$, m.p. $80\text{--}5\text{--}82^\circ$ (*picrate*, decomp. 201°). These condensations are anticipated from considerations of resonance. R. S. C.

Indigo. V. Benziminazole derivative isomeric with indigo. J. VAN ALPHEN (Rec. trav. chim., 1940, 59, 289—297; cf. A., 1939, II, 285).—2-Methylbenziminazole (I) (*phthalate*, m.p. 190°)

with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ (II) at 200° gives 2-1':3'-diketo-2'-hydrindylidenebenziminazole, m.p. $>350^\circ$ (nitrate, m.p. 184°), also obtained by boiling (I) with an excess of $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Heating (I) with isatin (III) or acenaphthenequinone gives 3-2'-benziminazolylmethyleneindoxyl, m.p. $>350^\circ$, and 7-keto-8-2'-benziminazolylmethylene-7:8-dihydroacenaphthene, m.p. 295° . 2-Ethyl- (phthalate, m.p. 197°) and 2-benzyl-benziminazole (IV) (phthalate, m.p. 177°) do not condense with (II), but (IV) and (III) at 180° give 3- α -2'-benziminazolylbenzylideneindoxyl, + EtOH, m.p. 264° . R. S. C.

Benzoyl derivatives of indigotin. V. H. DE DIESBACH, O. JACOBI, and C. TADDEI (Helv. Chim. Acta, 1940, 23, 469—484; cf. A., 1937, II, 78, 120).—Indigotin (I) is converted by hot BzCl into the substance (II) (Dessoulavy, Diss., Neuchâtel, 1909),



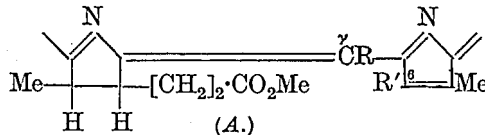
which is transformed by boiling NH_2Ph into $o\text{-NHBz-C}_6\text{H}_4\text{-CONHPh}$, m.p. 280° , 2:3-diphenylquinazolone, m.p. 159° , the quinoline derivative [(III), R = H], m.p. $255\text{--}256^\circ$, and a mixture of bases which gives a Bz₂ derivative, $\text{C}_{41}\text{H}_{27(29)}\text{O}_3\text{N}_3$, m.p. $\sim 300^\circ$, hydrolysed (conc. H_2SO_4) to a mixture of bases, $\text{C}_{27}\text{H}_{19(21)}\text{O}_3\text{N}_3$. This when diazotised and coupled with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ gives a dye, $\text{C}_{37}\text{H}_{26(24)}\text{O}_2\text{N}_4$, m.p. $215\text{--}255^\circ$. When the diazo-solution is kept it yields a ppt., $\text{C}_{27}\text{H}_{20}\text{O}_3\text{N}_2$, m.p. $>300^\circ$, the mother-liquors from which contain a stable diazo-salt which couples with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ to the product, $\text{C}_{37}\text{H}_{26(24)}\text{O}_3\text{N}_4$, m.p. 276° . The mixed bases and their derivatives are resistant to alkali at 400° and are either indifferent to oxidising agents or yield only $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Similar products are not formed from other primary aromatic amines. (II) and boiling $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ give a mixture separated by boiling EtOH-NaOEt into a compound [(III), R = Me], m.p. 264° , and an acid, $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2\text{H}_2\text{O}$, m.p. 210° , re-cyclised by heat or by solvents of high b.p. to the compound, $\text{C}_{23}\text{H}_{16}\text{ON}_2$, m.p. 263° . (II) and boiling $p\text{-C}_6\text{H}_4\text{Cl-NH}_2$ yield the quinoline derivative [(III), R = Cl], m.p. 293° , which loses Cl and suffers profound decomp. with alkali at 400° . $m\text{-C}_6\text{H}_4\text{Me-NH}_2$ and (II) afford benzoylanthranil-m-toluidide, m.p. 224° , which passes at 330° into 2-phenyl-3-m-tolyl-4-quinazolone, m.p. 139° . Similarly (II) and $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ at 200° afford benzoylanthranil- β -naphthalide, m.p. 258° , which passes at 300° into 2-phenyl-3-2'-naphthyl-4-quinazolone, m.p. 184° . (II) appears sometimes unchanged by boiling $o\text{-C}_6\text{H}_4\text{Me-NH}_2$, sometimes converted into ill-defined compounds; $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$ behaves similarly. Boiling *as-m*-xylidine and (II) give a compound, $\text{C}_{24}\text{H}_{16}\text{ON}_2$, m.p. 278° , and 2-phenyl-3-2':4'-dimethylphenyl-4-quinazolone, m.p.

130° (picrate, m.p. 202°). (II) passes slowly at $\sim 250^\circ$ into BzCl and Ciba-yellow. (I) and $o\text{-C}_6\text{H}_4\text{Cl-COCl}$ yield a mixture, m.p. 258° , converted by conc. H_2SO_4 into Höchst yellow U and a further similar dye with an additional Cl in the Ph nucleus. (I) and 2:4:6:1- $\text{C}_6\text{H}_2\text{Cl}_3\text{-COCl}$ give dichlorinated Höchst yellow U (IV), m.p. $>300^\circ$. H. W.

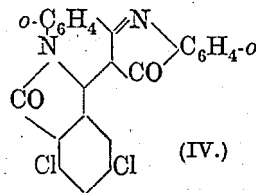
1:1'-Di(methylthiol)-3:3'-bisisoindolenylidene.—See B., 1940, 349.

Constitution of yeast ribonucleic acid. Guanineuridylic acid. J. M. GULLAND (Chem. and Ind., 1940, 321—324).—A reply to Tipson *et al.* (A., 1940, II, 27) concerning the entity of guanineuridylic acid. H. W.

Chlorophyll. XCV. Partial syntheses in the chlorin and purpurin series. H. FISCHER and M. STRELL (Annalen, 1940, 543, 143—161).—Purpurin 3 (= γ -formylpyrrochlorin) Me ester (I) (A., 1937, II, 470) with AcOH-HI at 70° , and subsequent reoxidation of the leuco-compound, gives γ -formylpyrroporphyrin Me ester, m.p. 246° (cf. A., 1940, II, 109); reduction with $\text{H}_2\text{-Pd}$ in COMe_2 affords mesopurpurin 3 Me ester, m.p. 155° . When (I) is shaken with a very large excess of 30% MeOH-KOH , γ -formyl-2-vinylpyrroporphyrin [Me ester, m.p. 208° (cryst. oxime)] is formed; short treatment with boiling conc. MeOH-KOH gives 2-vinylpyrroporphyrin. The amorphous oxime, m.p. 145° , of (I) is dehydrated by boiling $\text{Ac}_2\text{O} + \text{anhyd. K}_2\text{CO}_3$ (? NaOAc) to γ -cyanopyrrochlorin Me ester (II) (A, R = CN, R' = H), m.p. 205° ,



converted (HI) into pyrroporphyrin and γ -cyanopyrroporphyrin (III). The CN of (II) could not be hydrolysed; boiling 20% MeOH-KOH for 1 hr. affords (III). Catalytic reduction of (II) in AcOH gives first (30 hr.) the meso-compound and then decomp. products. Purpurin 7 Me₃ ester (IV), NH_2Et , and anhyd. K_2CO_3 in $\text{C}_5\text{H}_5\text{N}$ for 4 days (shaking) give a complex mixture of chlorins (a compound, m.p. 201° , is extracted by 10% HCl after treatment with $\text{Et}_2\text{O-CH}_2\text{N}_2$); purpurin 5 Me₂ ester (V) reacts similarly but (I) is largely unchanged. $\text{CH}_2(\text{CN})_2$ and (I) in $\text{C}_5\text{H}_5\text{N}$ at 100° (bath) yield $\gamma\text{-}\beta'\text{-}\beta'$ -dicyanovinylpyrrochlorin Me ester [A, R = $\text{CH}_2\text{C}(\text{CN})_2$, R' = H], m.p. 222° , decomposed by AcOH-HI . $\text{CH}_2(\text{CN})_2$, (V), and anhyd. Na_2CO_3 in $\text{C}_5\text{H}_5\text{N}$ at room temp./2 days give the compound, $\text{C}_{38}\text{H}_{38}\text{O}_4\text{N}_6$ [A, R = $\text{CH}_2\text{C}(\text{CN})_2$, R' = CO_2H (note hydrolysis)], m.p. $>320^\circ$, converted by hot $\text{C}_5\text{H}_5\text{N}$ into a compound resembling (spectrum) rhodochlorin, by MeOH-KOH into vinylrhodoporphyrin, and by AcOH-HI into a substance similar (spectrum) to chloroporphyrin e_5 Me₁ ester (VI); the neopurpurin reaction (A., 1939, II, 288; cf. A., 1940, II, 141) is negative. An extremely light-sensitive substance (extraction no. 22) is obtained from (IV), $\text{CH}_2(\text{CN})_2$, and NH_2Et in dioxan at 100° (bath). Anhyd. HCN and (V) in $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N} + \text{anhyd. K}_2\text{CO}_3$ give, after 5—6 days at room temp. and extraction of the Et_2O solution

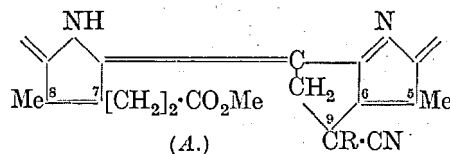


with 21% HCl (whereby hydrolysis of the original 6-CO₂Me may occur), the lactonic nitrile (as B), C₃₅H₃₅O₄N₅, m.p. >300°, converted by AcOH-HI into first a substance resembling (VI), and then rhodoporphyrin. Mesoporphyrin 5 and HCN react similarly. The cyanohydrin, C₃₄H₃₇O₃N₅, which eliminates HCN when heated, from (I) in C₅H₅N + anhyd. K₂CO₃, is hydrolysed (MeOH-HCl at room temp.) to ? Me₂ pyrrochlorin-γ-glycollate (A, R = OH·CH·CO₂Me; R' = H), m.p. 243° (can be benzoylated; free acid is unstable and loses HCO₂H when reduced to the meso-derivative), ? Me pyrrochlorin-γ-glycollamide, m.p. 215°, and γ-formylpyrroporphyrin. HCN and (IV) do not react. H. B.

Chlorophyll. XCVI. Total synthesis of phæoporphyrin a₅. H. FISCHER, E. STIER, and W. KANNGIESSER. **XCVII.** Synthesis of deoxophylloerythrin derivatives, an isomesoporphyrin, and an isorhodin. II. FISCHER and W. KANNGIESSER (Annalen, 1940, 543, 258–270, 271–287).—XCVI. γ-Formylpyrroporphyrin Me ester cyanohydrin (I) is converted by MeOH-HCl-SO₂ at 40°/48 hr. into Me₂ pyrroporphyrin-γ-glycollate (II), new m.p. 281°, and some (impure) Me₂ pyrroporphyrin-γ-glyoxylate (III) (cf. A., 1940, II, 109). Pyrroporphyrin-γ-glycollic acid (IV) with 2N-HCl at 70° gives γ-formylpyrroporphyrin (V) whilst isochloroporphyrin e₄ is similarly unaffected. Hydrolysis (conc. HCl at room temp.) of (I) and subsequent esterification (Et₂O-CH₂N₂) affords pyrroporphyrin-γ-glycollamide Me ester (VI), red, m.p. 252° (? 254°), and violet, m.p. 251°, forms (Zn salt, m.p. 319°), which is unaffected by C₅H₁₁·O·NO in COMe₂-2N-HCl at 0°—room temp. Boiling 2N-HCl converts (IV) into pyrroporphyrin but at 100° (bath), (IV) and (VI) give (V). Reduction [H₂, Pd-black, HCO₂H, 100° (bath)] of (VI), atm. reoxidation of the product, and esterification (CH₂N₂) affords pyrroporphyrin-γ-acetamide Me ester (VII), m.p. 318°, which loses NH₃ at 320° (bath) and yields phylloerythrin. Successive hydrolysis (15% HCl at 45°/48 hr.) and esterification (CH₂N₂) of (VII) gives isochloroporphyrin e₄ Me₂ ester (VIII). These results coupled with previous work (A., 1936, 1272) constitute a total synthesis of phæoporphyrin a₅. Oxidation (KMnO₄, COMe₂, C₅H₅N) of (II) yields (III) whilst reduction (H₂, Pd, HCO₂H, 90–95°; subsequent atm. reoxidation) of (III) affords (VIII) and a little (II).

XCVII. Oxidation (KMnO₄, C₅H₅N, room temp./3–4 days) of free phylloporphyrin gives pyrroporphyrin-γ-carboxylic acid (Me₂ ester, m.p. 242–244°), (V), and γ-hydroxymethylpyrroporphyrin. γ-Carbamylpyrroporphyrin Me ester, m.p. 287°, is obtained by successive hydrolysis (conc. H₂SO₄ at 70°) and esterification (MeOH-HCl) of the γ-CN-derivative. γ-Formylpyrroporphyrin Me ester (IX) and MeNO₂ in C₅H₅N-NH₂ afford γ-β'-nitrovinylpyrroporphyrin Me ester (+1 mol. of MeNO₂), m.p. 271°. γ-β'-Cyano-β'-carbomethoxyvinylpyrroporphyrin Me ester, m.p. 240° [from (IX) and CN·CH₂·CO₂Me in C₅H₅N + piperidine], when fused with (CH₂·CO₂H)₂

at 210°/3 min. yields 9-cyano-9-carbomethoxydeoxyphylloerythrin Me ester (A, R = CO₂Me), m.p. 246°, converted by 50% H₂SO₄ at room temp./2 days followed by Et₂O-CH₂N₂ into 9-cyanodeoxyphylloerythrin Me ester (A, R = H), m.p. 270°. γ-β'-



Cyano-β'-carbomethoxyvinylpyrroporphyrin Me ester (X) and CHN₂·CO₂Et at 100° (bath) give a compound, C₄₁H₄₅O₆N₅, m.p. 205–208°, which probably contains a cyclopropane ring. Reduction (H₂, PtO₂, dioxan) of (X) (as Zn salt), decomp. of the product (in Et₂O) with 20% HCl, and subsequent esterification (CH₂N₂) affords γ-β'-cyano-β'-carbomethoxyethylpyrroporphyrin Me ester, m.p. 238°, which is dehydrogenated to (X) in AcOH at 100° (bath)/3 hr., and is hydrolysed [20% HCl at 100° (bath)] to γ-β'-carboxyethylpyrroporphyrin (XI) (Me₂ ester, m.p. 202°). Dehydration of (XI) with H₂SO₄-oleum (cf. A., 1928, 1383) gives pyrroporphyrin-6:γ-propan-9-one [isomesorhodin] (XII) (as B) (Me ester, m.p. >325°, blackens ~248°) and isomesoverdin [better obtained from (XII) in AcOH at 50°, whereby loss of 2 H between C₍₁₀₎ and C₍₁₁₎ occurs], both of which form oximes (spectroscopic evidence).

H. B.
Derivatives of cyameluric acid. Probable structures of melam, melem, and melon. C. E. REDEMANN and H. J. LUCAS (J. Amer. Chem. Soc., 1940, 62, 842–846).—The Pauling-Sturdivant formula (cf. A., 1940, II, 110) for cyameluric acid (I) is confirmed by reactions which are often analogous to those of cyanuric acid. (I) gives salts, CuNH₄(C₆O₃N₇), NH₃ and Hg₃(C₆O₃N₇)₂. The K₃ salt (dried at 150°) and PCl₅ at 100°, later 139°, give cyameluryl trichloride (II) (93%), C₆N₇Cl₃, also obtained from (I) and PCl₅ at 218°. The anhyd. Na₃ salt and CH₂PhCl at 156° give tri-N-benzyl cyamelurate, m.p. 283–284° (corr.), hydrolysed by 6N-KOH to CH₂Ph·NH₂. With CH₂Ph·OH, (II) gives CH₂PhCl and (I). CH₂N₂ and (I) give Me, C₆H₂O₃N₇Me, and on further treatment Me₃ cyamelurate, C₆O₃N₇Me₃, +1.5H₂O. With 15N-NH₃, NH₃-Et₂O, or liquid NH₃, (II) gives mixtures. Probably melam is [3:5-C₃N₃(NH₂)₂]₂NH, melem is C₆H₇(NH₂)₃, and melon is a large, planar, cyclic polymeride with C-N-C linkings.

R. S. C.
Wing-pigments of butterflies. V. Degradation of deiminoleucopterin. H. WIELAND and A. TARTER (Annalen, 1940, 543, 287–292).—The material pptd. by Et₂O from the solution obtained from deiminoleucopterin (A., 1933, 1310) and Cl₂ in MeOH at ~0°, when crystallised from H₂O, gives deiminoleucopterin glycol Me₁ ether, C₂₂H₂₆O₁₉N₁₂·3H₂O, darkens ~150°, no decomp. up to 260°; the main reaction product (Et₂O-sol.; yield increased by less rigorous cooling) is Me 5-methoxy-uramil-7-oxalate,

$\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C}(\text{OMe}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Me}$, m.p. 195°, which is hydrolysed (boiling 3N-HCl) to MeOH (2 mols.) and 1 mol. each of NH_3 , $\text{H}_2\text{C}_2\text{O}_4$, and alloxan. H. B.

α -Di-4-morpholinoethane.—See B., 1940, 347.

Absorption spectra of N-substituted auramine dyes. G. BREUER and J. SCHNITZER (J.C.S., 1940, 461—463).—The absorption spectra of auramine, N-phenyl-, N- α -naphthyl-, N- β -naphthyl-, and N-2-anthryl-auramine, their hydrochlorides and picrates (except that of N-2-anthrylauramine) are recorded over the range 2500—5500 Å. A. J. M.

Polarisation in heterocyclic rings with aromatic character. V. Substitution of aromatic hetero-rings with directly united phenyl chain. E. OCHIAI, Y. TUNODA, I. NAKAYAMA, and G. MASUDA (J. Pharm. Soc. Japan, 1939, 59, 228—235).—4-Phenyl-5-methylthiazole, b.p. 110—111°/2 mm. (hydrobromide, m.p. 197°; picrate, m.p. 124—125°), from $\text{HCS} \cdot \text{NH}_2$ and α -bromopropiophenone, is converted by HNO_3 - H_2SO_4 at 0° into 4-p-nitrophenyl-5-methylthiazole, m.p. 98°, in 90% yield; it is oxidised by KMnO_4 to p- NO_2 - C_6H_4 - CO_2H and hydrogenated to 4-p-aminophenyl-5-methylthiazole, m.p. 80° (acetate, m.p. 144°). Under similar conditions 4-phenylthiazole affords 4-p-nitrophenylthiazole, m.p. 180° (96% yield), reduced to 4-p-aminophenylthiazole, m.p. 99° (acetate, m.p. 165°). 4 : 5-Diphenyl-2-methylthiazole, m.p. 51—52°, yields 4 : 5-di-p-nitrophenyl-2-methylthiazole, m.p. 183°. Regardless of the type of thiazole, NO_2 always enters the p-position in the C_6H_5 nucleus and is not influenced by the position of the nucleus. Nitration of 2 : 5-diphenylpyrazine yields two isomeric 2 : 5-dinitrophenylpyrazines, m.p. 172—173° and decomp. 292°, respectively; since they are resistant to oxidation their constitution has not been established but they are not identical with 2 : 5-di-m-nitrophenylpyrazine, m.p. 249°, obtained from m-nitro- ω -aminoacetophenone. 2-Phenyl-4 : 6-dimethylpyrimidine (I) reacts only slowly with HNO_3 - H_2SO_4 at 0°, giving a small amount of a (NO_2)₁-compound, m.p. 155—156°; this is catalytically reduced to the (NH_2)₁-derivative, m.p. 88—90° (picrate, decomp. 199—200°; acetate, m.p. 130—132°), which gives a (OH)₁-compound, m.p. 125—127°, not identical with 2-p-hydroxyphenyl-4 : 6-dimethylpyrimidine. Fuming HNO_3 in AcOH transforms (I) into a compound, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_6$, m.p. 167—170°. 2-Phenyl-4 : 6-distyrylpyrimidine, from (I), PhCHO, and ZnCl_2 at 150°, has m.p. 158.5—159°. H. W.

Sulphur derivatives of pyridine. (Synthesis of 2 : 3-pyridothiochromanone.) M. COLONNA (Gazzetta, 1940, 70, 154—159).—5-Nitro-2-pyridylthiolacetic acid, m.p. 105° [obtained from 5-nitro-2-thiopyridine (I), KOH, and $\text{CH}_3\text{Cl} \cdot \text{CO}_2\text{K}$ in the water-bath, or better from 2-chloro-5-nitropyridine and $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and NaHCO_3 in EtOH at the b.p.], with conc. H_2SO_4 at 150—180° gives a thioindigo derivative, not isolated. β -(5-Nitro-2-pyridyl)thiolpropionic acid, m.p. 125° [obtained from a neutralised mixture of (I) and $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ heated at 100° for 3 hr.], with PCl_5 followed by AlCl_3 in C_6H_6 at the b.p. gives 5'-nitropyrido-2' : 3'-3 : 2-thiochromanone, m.p.

107°. 5 : 5'-Dinitro-2 : 2'-dipyridyl sulphide with $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 in AcOH gives the corresponding sulphone, m.p. 185—187°. E. W. W.

Cyanine dyes.—See B., 1940, 406, 408.

Polarisation in heterocyclic rings with aromatic character. VIII. Polarisation in the benzene ring. E. OCHIAI and T. NISHIZAWA (J. Pharm. Soc. Japan, 1940, 60, 43—48).—The activity of C_{22} in thiazole towards nucleophilic reagents is paralleled by that of C_{11} in benzthiazole (I). NaNH_2 and (I) in decahydronaphthalene at 140° afford (mainly) 1-aminobenzthiazole, m.p. 130° (monoacetate, m.p. 187°; hydrochloride, decomp. 235—236°; picrate, m.p. 265°), 2 : 2'-diaminodiphenyl disulphide, m.p. 93° (Ac_2 derivative, m.p. 169°), and a compound, m.p. 194°, possibly a dibenzthiazolyl or dibenzthiazole, which does not yield a picrate. 1-Methylbenzthiazole (II) condenses with PhCHO and ZnCl_2 at 160—170° to 1-styrylbenzthiazole, m.p. 111—112°, reduced (Pd-C in EtOH) to 1- β -phenylethylbenzthiazole, b.p. 180° (bath)/0.5 mm., m.p. 62°. 1-Aminobenzthiazole (III) and CH_2BzBr in EtOH at 100° afford benzthiazolo-1' : 2'-2 : 1-4-phenylglyoxaline hydrobromide, m.p. 263° (corresponding base, m.p. 100°). CH_2BzBr and (II) readily give the product, $\text{C}_{16}\text{H}_{14}\text{ONBrS}$, m.p. 233°, which with NaHCO_3 yields a very unstable material which passes into a red, amorphous mass; this gives the red diazo-reaction and a bluish-violet Ehrlich test. A uniform product is likewise not obtained from (II) and CH_2AcCl . Picryl chloride and (III) yield 1-picramidobenzthiazole, m.p. 205°, which in boiling PhNO_2 evolves nitrous fumes and gives benzthiazolo-1' : 2'-2 : 1-4 : 6-dinitrobenziminazole, m.p. 243°. (I), from o- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SH}$ and HCO_2H in presence of a little H_3BO_3 , gives a picrate, m.p. 168°, and perchlorate, m.p. 135°. (II), obtained as above but by use of Ac_2O , affords a picrate, m.p. 153.5°. (III), m.p. 130° (hydrochloride, decomp. 236°; acetate, m.p. 187°), is obtained by bromination of $\text{NHPh} \cdot \text{CS} \cdot \text{NH}_2$ or by catalytic reduction (Pd-C in AcOH) of o- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CNS}$.

H. W.

Preparation of quinine iodo-hydriodide. S. N. NAUMOV and C. B. MEDINSKI (Acta Univ. Asiæ Mediæ, 1937, [vi], No. 32, 1—6).—20 g. of KI in 100 ml. of H_2O are added to a solution of quinine sulphate 5, H_2SO_4 5, and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ 30 g. in 800 ml. of H_2O , and the product is twice recryst. from 1% H_2SO_4 in 85% EtOH. R. T.

Alkaloids of Stemona tuberosa, Loureiro. II. Tuberostemonine. H. KONDO, K. SUZUKI, and M. SATOMI. IV. Stemonidine. K. SUZUKI (J. Pharm. Soc. Japan, 1939, 59, 177—186).—II. Tuberostemonine (I) has been obtained as the cryst. hydrobromide, m.p. 120° (decomp.), aurichloride, and perchlorate, m.p. 242° (decomp.), from which the cryst. base, $\text{C}_{22}\text{H}_{33}\text{O}_4\text{N}$ (not $\text{C}_{19}\text{H}_{29}\text{O}_4\text{N}$), m.p. 86—88° [or, + 1MeOH, m.p. 65—88° (decomp.)], is isolated. (I) is a non-phenolic, tert. base devoid of OMe, NMe, or active H. It contains a lactone group but does not react with NH_2OH or p- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$. It yields a methiodide (+ H_2O), m.p. 236—238° (decomp.), methochloride, (+ $2\text{H}_2\text{O}$), m.p. 172°, methylmethosulphate, m.p. 253° (decomp.), and a methylauri-

chloride (+H₂O), m.p. 140° after softening at 125°. (I) is not affected by Ac₂O in CO₂ but under the customary conditions it is converted into a neutral, amorphous substance which gives Ehrlich's pyrrole reaction in the cold. (I) is unaffected by boiling 30% H₂SO₄ or by HCl-EtOH. The function of 2 O in (I) is not elucidated. Dry distillation of (I) with Zn dust gives vapours which turn a pine shaving moistened with HCl red; this reaction is not given by the base itself. Oxidation with Ag₂O leads to a neutral compound, C₂₂H₂₉O₄N, m.p. 178°, which contains a lactone group and gives Ehrlich's pyrrole reaction. (I) therefore contains a pyrrolidine ring which is dehydrogenated to a pyrrole ring. Attempts to obtain an additive product with maleic anhydride were unsuccessful. Possibly (I) is identical with the alkaloid, C₂₂H₃₃O₄N, m.p. 86–87°, from *Stemona sessilifolia* (Schild, A., 1936, 350) although (I) cannot be catalytically hydrogenated (PtO₂ in EtOH) and does not give a cryst. dehydrogenated product when treated with I or MeI according to Schild.

IV. Stemonidine (II) is a *tert.* base since it does not react with Zerevitinov's reagent or Ac₂O and does not give Liebermann's reaction. Complete analysis of the compound, m.p. 248°, shows it to be the methiodide. Of the 5 O of (II) two are present in a lactone and one in a OMe group; the function of the remaining two is unknown. Distillation of (II) with Zn dust gives a pyrrole derivative which is readily hydrogenated (Pd-C in AcOH) to a liquid base; probably the pyrrole nucleus is not preformed in (II). I or MeI converts (II) into the hydriodide or methiodide; dehydrogenation does not appear to take place. Oxidation of (II) by KMnO₄ (=3 O) in COMe₂ gives a base characterised by a *methiodide*, C₁₉H₂₉O₅N.MeI, m.p. 235°. Aq. KMnO₄ (=7.9 O) in H₂O at 60° gives a quaternary base (*aurichloride*, C₁₉H₂₉O₅NMeAuCl₄, m.p. 158°). When oxidised by KMnO₄ (=13.5 O) in dil. H₂SO₄ at 10° (II) yields a neutral substance (III), C₁₆H₂₃O₅N, m.p. 208°, [α]_D²⁰ –58.3°, and a compound (IV), C₁₁H₁₇O₄N, m.p. 202°, [α]_D²⁰ –24.17° (*semicarbazone*, m.p. 258°). (III) contains a lactone group and OMe but is not a pyrrole derivative and does not react with CO₂ reagents. (IV) contains OMe but is not a lactone; it strongly reduces ammoniacal Ag solution but does not give the pyrrole reaction. 25% HCl-AcOH and EtOH saturated with HCl are without action on (II). Dehydrogenation of (II) by 40% Pd-asbestos at 260–290° gives a non-cryst. dehydro-base (which contains OMe and a lactone group, gives the diazo-reaction, and yields an *oxime* and a *methiodide*, C₁₇H₂₃O₄N.MeI, decomp. 227–228°), a neutral pyrrole derivative which gives the pine shaving and Ehrlich reaction, and an (impure) acid which gives a dark green colour with FeCl₃.

H. W.

Alkaloids of fumariaceae plants. XXIV. *Corydalis ochotensis*, Turcz. XXV. *Corydalis pallida*, Pers. R. H. F. MANSKE (Canad. J. Res., 1940, 18, B, 75–79, 80–83).—XXIV. The following substances have been isolated: protopine (I), cryptocavine, ochotensine, aurotensine, ochotensimine (*methiodide*, decomp. 225°, [α]_D²² +49.2° in MeOH, identical with Me ether methiodide of ochotensine;

dihydromethine, C₂₃H₂₇O₄N, m.p. 92°), alkaloid F 49, C₁₉H₂₃O₄N, m.p. 228° (decomp.), fumaric acid, and maltol (?).

XXV. Capaurine, *d*- and *dl*-tetrahydropalmitine, (I), capauridine, capaurimine (F 50), C₂₀H₂₃O₅N, m.p. 212°, [α]_D²⁴ –287° in CHCl₃ (phenolic; one OH and three OMe), and alkaloid F 51, C₂₀H₂₃O₄N, m.p. 171° (one OH and three OMe), have been isolated. Methylation of capaurimine gives capaurine *O*-Me ether, the *dl*-form of which is identical with capauridine *O*-Me ether, and alkaloid F 51 similarly affords *dl*-tetrahydropalmitine, not identical with the known *dl*-bases of the same formula.

F. R. S.

Conessine series. V. Reduction of nitroconessine to conessineoxime and conversion of the oxime into mono[hydr]oxyconessine. S. SIDDIQUI and V. SHARMA (Proc. Indian Acad. Sci., 1939, 10, A, 417–422; cf. A., 1937, II, 527).—Hydrogenation (Pt-black in MeOH at room temp.) of nitroconessine gives *conessineoxime* (I), C₂₁H₄₁ON₃, m.p. 230–232°, [α]_D²⁰ –26.3° in abs. EtOH, +9.5° in CHCl₃, better obtained by use of an excess of Na-Hg in EtOH-AcOH. (I) yields a *carbonate*, C₂₁H₄₁ON₃·2H₂CO₃·4.5H₂O, m.p. >360°, *dihydrochloride*, m.p. 349° (decomp.), *dihydriodide*, m.p. 331°, *picrate*, m.p. 254° (decomp.) after blackening at 251°, *platinichloride*, m.p. 292°, and *methiodide*, m.p. 258° (decomp.) after changing colour at 242°. (I) is transformed by HNO₂ into N₂O and monohydroxyconessine (II), m.p. 200°, [α]_D²⁰ +11.5° in EtOH, also produced from (I) and CH₂O-HCO₂H at 100°. (I) and Br (=2 atoms) appear to yield a Br-derivative. (III) is converted by Br into a product, decomp. 232° after shrinking at 200°, which is transformed by prolonged heating with EtOH or H₂O into monohydroxyconessine dihydrobromide.

H. W.

Constitution of matrine. XXII. Gen-alkaloids of matrine and *d*-lupanine. E. OCHIAI, Y. ITO, and M. MARUYAMA (J. Pharm. Soc. Japan, 1939, 59, 270–273; cf. A., 1939, II, 460).—*N*-isoAmyl-piperidine or 2-methylindolizidine and 3% H₂O₂-COMe₂ give *oxides*, m.p. 135° (+0.75H₂O) (*picrate*, m.p. 117°), and an oil (*picrate*, m.p. 164°), respectively, but *N*-isoamylpiperidone, treated similarly, is unchanged. *d*-Lupanine (I) and 3% H₂O₂ give a monoxide (*dipicrate*, m.p. 189°; *perchlorate*, m.p. 247°; *aurichloride*, m.p. 216°; *methiodide*, m.p. 137°) [cf. matrine (II)]. (I) and PCl₅-K₂S in xylene give *d*-thiol-lupanine, m.p. 102° (*picrate*, m.p. 225°), but (II) is unchanged by similar treatment. The lactam ring of (I) is not broken by KOH-EtOH, but (II) is hydrolysed.

A. T. P.

Menispermaceae alkaloids (formerly, alkaloids of *Sinomenium* and *Cocculus*). L. Alkaloids of *Stephania Sasakii*, Hayata. I. M. TOMITA (J. Pharm. Soc. Japan, 1939, 59, 207–208; cf. Kondo *et al.*, A., 1939, II, 459).—The following are obtained from the roots of *S. Sasakii*: (a) a cryst. base, decomp. 103° (as C₆H₆ adduct), which agrees in chemical reactions and physical consts. with cepharanthine and is degraded (Hofmann) to cepharanthine-α- and -β-methine; (b) a base (I), C₃₈H₄₀O₇N₂, m.p. 115–117°, [α]_D²⁰ –57.4° in CHCl₃ [*hydrochloride* (+2H₂O), m.p. 222–225° (decomp.)],

which is insol. in aq. NH_3 , alkali carbonate or hydroxide and contains 4OMe. The *methiodide*, m.p. 220° , is transformed by hot alkali hydroxide into the *methine* base, $\text{C}_{40}\text{H}_{44}\text{O}_7\text{N}_2\cdot\text{H}_2\text{O}$, m.p. $110-114^\circ$, $[\alpha] \pm 0^\circ$; (c) a phenolic base (II), $\text{C}_{36}\text{H}_{36}\text{O}_7\text{N}_2$, m.p. 210° , $[\alpha]_{\text{D}}^{20} -36.7^\circ$ in CHCl_3 (*hydrochloride*, m.p. 264°), which contains 2 OMe and is converted by CH_3N_2 into a *Me₂ ether*, m.p. $160-165^\circ$, with 4 OMe which differs from (I). (I) and (II) are very similar chemically, particularly in their colour reactions. H. W.

Organic arsenicals.—See B., 1940, 404, 406.

Gallium triphenyl. H. GILMAN and R. G. JONES (J. Amer. Chem. Soc., 1940, 62, 980-982).—*Ga triphenyl* (prep. in 82% yield from HgPh_2 and Ga in N_2 at 130°), m.p. 166° , is moderately reactive. With PhCHO in boiling C_6H_6 it gives 70% of $\text{CHPh}_2\cdot\text{OH}$. With $\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$ it gives 85% of $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}_2$. With BzCl in C_6H_6 it gives 79% and in light petroleum 68.4% (as oxime) of COPh_2 (cf. TiPh_3 , which gives only TiPh_2Cl). It does not react with COPh_2 (3 mols.) in boiling xylene, but an excess of GaPh_3 gives 35% of CHPh_3 . With CH_2PhCl it gives an oil containing CH_2Ph_2 (yields 9% of COPh_2). It does not react with PhCN . It gives no colour with Michler's ketone in C_6H_6 , unless it is present in excess; it probably forms a complex with the NMe_2 . R. S. C.

Reaction of mercuric acetate with *p*-phenetidine and *p*-anisidine. M. RAGNO (Annali Chim. Appl., 1940, 30, 72-78).—*p*-Phenetidine with $\text{Hg}(\text{OAc})_2$ in AcOH-EtOH yields an *adduct*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{Hg}(\text{OAc})_2$, m.p. 137° ; similarly treated, *p*-anisidine yields 3-*acetomercuri-p*-anisidine-*N*-*mercuriacetate acetate*, m.p. $148-149^\circ$ (decomp.), which with aq. KI affords 3-*mercuri-p*-anisidine *iodide* and, with aq. KBr, the corresponding *bromide* (I), m.p. 165° . The structure of the compounds is indicated by bromination of (I) to 3:5-dibromo-anisidine. F. O. H.

[Preparation of] organic mercury derivatives of basic triphenylmethane dyes. L. CHALKLEY (Science, 1940, 91, 300; cf. A., 1925, i, 1108; 1929, 1322).—Derivatives of the basic dye are mercurated, and then converted into the dye, e.g., 4:4'-bis-dimethylaminotriphenylacetone nitrile is readily mercurated, and the mercurated nitrile converted into the corresponding Hg malachite-green by means of a photochemical reaction. The Hg in this compound is relatively stable to $(\text{NH}_4)_2\text{S}$ which, in presence of aq. NH_3 , gives an org. Hg^{II} sulphide. L. S. T.

Mercuration of cholesterol. R. H. LEVIN and M. A. SPIELMAN (J. Amer. Chem. Soc., 1940, 62, 920-921).—The product, m.p. $200-205^\circ$, obtained (Merz, A., 1926, 723) from cholesterol by $\text{Hg}(\text{OAc})_2\text{-AcOH}$, is the 6-HgCl-derivative, since the derived 6-iodocholesterol, m.p. $156-158^\circ$ (*benzoate*, m.p. $214-215^\circ$), is hydrolysed by $\text{CuCl}_2\text{-NaHCO}_3\text{-H}_2\text{O}$ at 225° (not by milder reagents) into 6-ketocholestanol (3:5-dinitrobenzoate, m.p. $226-228^\circ$), isolated as benzoate. R. S. C.

Hydroxyquinolines. IV. Mercurated derivatives of 8-hydroxyquinoline. F. PIRRONE (R. C. Atti Accad. Ital., 1939, [vii], 1, 50-54).—8-Hydroxy-

quinoline (I) heated in AcOH with $\text{Hg}(\text{OAc})_2$ (II) gives its ?-*acetatomercuri*-derivative, m.p. $<360^\circ$, which with HCl gives a compound, $\text{C}_9\text{H}_6\text{ONHgCl}$, m.p. 205° , and with aq. NH_3 a compound, $\text{C}_9\text{H}_7\text{O}_2\text{NHg}$. In H_2O , (I) and excess of (II) give 8-*hydroxy-?-bisacetatomercuriquinoline*. If the AcOH formed is progressively neutralised by NaOH, the Na derivative of the ???-trisacetatomercuri-derivative is obtained. E. W. W.

Chemical structure in the protein series. A. WEIDINGER (Collegium, 1940, 1-37).—A review.

Melanins, their chemistry and significance. W. L. C. VEER (Chem. Weekblad, 1940, 37, 214-222).—A review. S. C.

Effect of denaturing agents on myosin. I. Sulphydryl [thiol] groups as determined by porphyrindin titration. J. P. GREENSTEIN and J. T. EDSALL. II. Viscosity and double refraction of flow. J. T. EDSALL and J. W. MEHL (J. Biol. Chem., 1940, 133, 397-408, 409-429).—Amplification of previous work (A., 1939, III, 869). The porphyrindin titration and the significance of η for solutions of large, very asymmetrical mols. are discussed. The chemical and physical effects are uncorrelated. Methionine + cysteine account for 95% of the S of myosin. R. S. C.

Number of peptide linkages in insulin.—See A., 1940, III, 498.

Gas-volumetric semi-micro-determination of carbon. Wet method for aliphatic and cyclic compounds. E. BERL and W. KOERBER (Ind. Eng. Chem. [Anal.], 1940, 12, 245-246).—The sample is oxidised with H_2CrO_4 and a Hg catalyst, and the CO_2 evolved is measured in a gas burette. J. D. R.

Determination of chlorine, bromine, and iodine in organic compounds by hydrogenation. A. SLOOFF (Rec. trav. chim., 1940, 59, 259-283).—Cl, Br, and/or I in org. compounds are determined by heating the compound in H_2 , passing the vapours over Ni foil at 800° , absorbing the HHal in solid Na_2CO_3 , and (after destruction of NaCN and NaCNS, if necessary) titrating the Na halide formed. In 31 cases the error is $<0.4\%$. Published data are used to show by calculation that decomp. of HCl and HBr in excess of H_2 is negligible and that at 800° there is 2% of dissociation of HI, which, however, is reduced to $<1\%$ (considered negligible) by cooling to 700° . R. S. C.

Determination of elements in organic substances. L. ROSENTHALER (Pharm. Acta Helv., 1939, 14, 215-216; cf. A., 1937, II, 358).—Cl and Br are liberated from many org. compounds by treatment with saturated aq. KMnO_4 and H_2SO_4 . Cl may be detected with $m\text{-C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$ (forms at first drops, then needles, and finally aggregates; Br does not react) and Br with fluorescein paper. Numerous compounds which liberate H_2S by the action of nascent H are described. In some cases, e.g., EtSO_3Na , cystine, cysteine, a positive reaction [with $\text{Pb}(\text{OAc})_2$] is obtained but no H_2S is evolved. The liberation of CO_2 by the action of H_2SO_4 on org. substances is also discussed. E. H. S.

Determination of organic nitrogen. J. CARTIAUX (Ann. Chim. Analyt., 1940, [iii], 22, 92).—N is converted into NH_4^+ by treatment of the sample with 5 c.c. of conc. H_2SO_4 and two to four 10–20-c.c. portions of H_2O_2 in the manner described. The method gives better results than the usual $\text{H}_2\text{SO}_4 + \text{Hg}$ attack, and is particularly suitable for leather, wool, tobacco, and vegetable products. L. S. T.

Electrolytic method of oxidising arsenic and phosphorus for their determination in organic compounds. C. B. DI CAPUA (Atti X Congr. Internaz. Chim., 1938, III, 401–406).—The compound is dissolved in 70% H_2SO_4 and the solution introduced into a sintered glass crucible dipping into 70% H_2SO_4 . The solution is then electrolysed using a Pt wire anode immersed in the crucible and a Pt foil cathode in the outer vessel. The H_3AsO_4 and H_3PO_4 produced are subsequently pptd. as $\text{MgNH}_4\text{AsO}_4$ and MgNH_4PO_4 , respectively. J. W. S.

Identification of paraffins. Analysis of paraffinic mixtures by means of Raman spectra. A. V. GROSSE, E. J. ROSENBAUM, and H. F. JACOBSON (Ind. Eng. Chem. [Anal.], 1940, 12, 191–194).—The sample is freed from aromatic and ethylenic constituents, carefully fractionated, and the Raman spectra of the individual narrow cuts are photographed. For qual. analysis this spectrum is matched with the characteristic lines of pure isomerides known to be present in the mixture. Quant. analysis is carried out, with an accuracy of 5–10%, by visual estimation of the relative intensities of the Raman lines. The method has been applied to the isomeric pentanes, hexanes, and heptanes, and to mixtures prepared by the addition of olefines to paraffins in presence of AlCl_3 . J. D. R.

Colorimetric determination of primary mononitroparaffins. E. W. SCOTT and J. F. TREON (Ind. Eng. Chem. [Anal.], 1940, 12, 189–190).—A sample of aq. EtNO_2 is treated with NaOH , acidified (HCl), and aq. FeCl_3 added. The red colour produced is compared colorimetrically with a standard solution of similar concn. The method succeeds with PrNO_2 and BuNO_2 , but with Pr^sNO_2 and Bu^sNO_2 the colour fades too rapidly, whilst with MeNO_2 no colour is produced. J. D. R.

Oxidation with dichromate and its micro-analytical applications. I. General principles. II. Micro-determination of ethyl alcohol. L. THIVOLLE and G. SONNTAG (Bull. Soc. Chim. biol., 1939, 21, 1353–1368, 1369–1380).—I. Oxidisable substances are determined in strongly acid medium by adding a 2–3 c.c. excess of $\sim 0.1\text{N-K}_2\text{Cr}_2\text{O}_7$ and a few drops of 0.1% diphenylbenzidine in 70% H_2SO_4 and titrating with 0.002N- $\text{K}_4\text{Fe}(\text{CN})_6$ until the colour vanishes.

II (cf. Nicloux *et al.*, A., 1935, 116; 1936, 535; 1937, II, 317). EtOH is oxidised in the cold with excess of $\text{K}_2\text{Cr}_2\text{O}_7$ in HNO_3 and the excess is titrated as above. The error is $\pm 0.5\%$ when the amount of EtOH is 1–3 mg. or 1–2% when it is < 0.5 mg.

W. MCC.

Rapid qualitative test for alcoholic hydroxyl group. Use of nitrate- and perchlorato-

cerate anions as test reagents. F. R. DUKE and G. F. SMITH (Ind. Eng. Chem. [Anal.], 1940, 12, 201–203).—The test substance in H_2O is treated with a solution of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (I) in aq. HNO_3 or $\text{H}_2\text{Ce}(\text{ClO}_4)_6$ (II) in aq. HClO_4 . A red colour indicates an alcohol. With substances insol. in H_2O a solution in dioxan is employed and (II) cannot be used because of reduction of the reagent. Acids, aldehydes, ketones, esters, and hydrocarbons do not interfere. Amines, amine hydrochlorides, substances with chromophoric groups, readily oxidisable substances, and phenols interfere. Aq. solutions of 2–4% BuOH give positive tests with (I) and 1–2% with (II).

J. D. R.

Hydroxamic acids in qualitative organic analysis. D. DAVIDSON (J. Chem. Educ., 1940, 17, 81–84).—Tests involving the formation of hydroxamic acids are described for alcohols, ethers, aldehydes, esters, carboxylic and sulphonic acids, phenols, oximes, NO_2 -compounds, amides, acid chlorides, and anhydrides.

L. S. T.

Detection of organic compounds. L. ROSENTHALER (Pharm. Acta Helv., 1939, 14, 218–221).—(a) MeOH does not react with HNO_3 (65%) at room temp. (differentiation of MeOH and EtOH). (b) The reaction depending on the formation of a blue colour from glycerol with $\text{K}_2\text{Cr}_2\text{O}_7$ and HNO_3 is not sp.; many other alcohols and sugars react similarly. (c) For the identification of phenols the colour of the melt and the alkali solution of the reaction product with *o*-sulphobenzoic anhydride is a very sensitive test. 15 examples are given. (d) By the use of Na alizarinsulphonate as indicator, the formation of H ions by the action of neutral Hg salt solutions on HCN can be detected in 1 $\mu\text{g.}$ of HCN per c.c. An improvement on the Vortmann method is given. The sample is heated with aq. NaOH and FeSO_4 , the mixture is filtered, acidified, NaNO_2 is added, and, after warming and cooling, aq. NH_3 and $(\text{NH}_4)_2\text{S}$ are added (nitroprusside reaction). (e) Characteristic light brown, ball-shaped masses are formed when a solution of theophylline in aq. NH_3 is treated with solid TlOAc . (f) The blue colour formed from aromatic *o*-(OH)₂-compounds and K_2CO_3 and FeSO_4 is discussed. Ascorbic and dihydroxymaleic acids react similarly but the reaction mixture is decolorised by HCl . (g) The oxidation of many org. compounds by $\text{Fe}_2(\text{SO}_4)_3$ is detected by the reaction of the Fe^{3+} formed (after addition of H_3PO_4) with $(\text{CMe}_2\text{N.OH})_2$ and aq. NH_3 . 2.5 c.c. of a solution containing 1 $\mu\text{g.}$ of pyrocatechol give a positive reaction. E. H. S.

Detection of small amounts of mustard gas. A. S. JOUSMA (Pharm. Weekblad, 1940, 77, 246–249).—Mustard gas (I) is adsorbed on a granule of active C, which is then heated (below redness) in a stream of H_2 washed with KMnO_4 solution to remove H_2S , and the gas is passed over a red-hot Pt wire and through a paper containing $\text{Pb}(\text{OAc})_2$, on which a brown or black stain is produced. The method is very sensitive and will detect (I) in C which has been exposed to the vapour for only 5 sec. S. C.

Analytical procedures employing Karl Fischer reagent. IV. Determination of acid anhydrides.

D. M. SMITH, W. M. D. BRYANT, and J. MITCHELL, jun. (J. Amer. Chem. Soc., 1940, **62**, 608—609; cf. A., 1940, II, 146).—A procedure for the determination of carboxylic anhydrides (described) depends on the complete hydrolysis of the anhydride to acid in presence of excess of H_2O , and subsequent titration of the residual H_2O with Karl Fischer reagent. The method is best suited for acyclic aliphatic anhydrides. Analytical data are recorded for ten anhydrides.

W. R. A.

Potentiometric determination of glucose with potassium ferricyanide in sodium carbonate solution. H. T. S. BRITTON and L. PHILLIPS (Analyst, 1940, **65**, 149—152).— $K_3Fe(CN)_6$ in $\sim 0.4M$ aq. Na_2CO_3 can be titrated potentiometrically with glucose solution at $92-94^\circ$. The inflexion in the potential curve extends over $0.4-0.5$ v. 1 mol. of glucose requires 5.9 mols. of $K_3Fe(CN)_6$ for oxidation.

J. W. S.

Micro-determination of glucose, free and conjugated glucuronic acid. I. Determination of free and conjugated glucuronic acid in presence of glucose in aqueous solution. S. KAKINUMA (J. Pharm. Soc. Japan, 1939, **59**, 244—246).—This is effected by the method of Ogata *et al.* (*ibid.*, 1929, **49**, 541) after first removing the glucose ($\geq 1\%$) by yeast.

R. S. C.

Objective microphotometry. Photometric analysis of picrates of organic bases. P. KRUMHOLZ and E. KRUMHOLZ (Natuurwetensch. Tijds., 1940, **22**, 27—28).—The picrate of a base or of a hydrocarbon (*e.g.*, anthracene) is heated with $0.2N$ $NaOH$ in 80% $EtOH$ and the Na picrate determined microphotometrically. The error is $\sim 0.5\%$. S. C.

Determination of primary, secondary, and tertiary amines and ammonia present together. K. G. MIZUTSCH and A. J. SAVITSCHENKO (Prom. Org. Chim., 1940, **7**, 24—25).—The mixture of hydrochlorides is dissolved in 30 ml. of H_2O , and 25 ml. of $EtOH$ are added, followed by 3 g. of $NaNO_2 \cdot Co(NO_2)_2$ in 50 ml. of H_2O at 0° . The ppt. of NH_4 cobaltinitrite is collected after 15 min., washed with $EtOH$, and NH_3 determined in the usual way. Primary amines are determined as the difference between total NH_2-N as found by Van Slyke's method and NH_3-N . *tert.* Amine is determined by Kjeldahl distillation after treating the solution with excess of HNO_2 (2 hr. at $15-20^\circ$). *sec.* Amines are given by difference between total N and NH_3 , NH_2 , and *tert.* amine-N.

R. T.

Colorimetric micro-determination of arginine and of mono-substituted derivatives of guanidine. Application to protein hydrolysates. C. DUMAZERT and R. POGGI (Bull. Soc. Chim. biol., 1939, **21**, 1381—1388; cf. Jean, A., 1934, 672).— $EtOH$ -glycerol mixture is added, after addition of aq. $NaOH$, α - $C_{10}H_7OH$, and $NaOBr$, and the arginine in 2 c.c. of protein hydrolysate is determined by a modification of Weber's method (A., 1930, 755). The error is $\pm 2\%$. A colorimeter or step photometer is used. Since the reaction is not usually affected by the nature of the substituent when one NH_2 only of guanidine is substituted, methylguanidine, agmatine, octopine, synthalin (I), and arcaine (II) are

determined in the same way, (I) and (II) yielding colour intensity double that given by equiv. amounts of the other substances. W. McC.

Azides as reagents for the identification of organic compounds. XVII. *p*-Nitrobenzazide and *p*-nitrophenylcarbimide as reagents for identification of amines. P. P. T. SAH (Rec. trav. chim., 1940, **59**, 231—237; cf. A., 1940, II, 32).—*p*-Nitrobenzazide or $p-NO_2 \cdot C_6H_4 \cdot NCO$ in $PhMe$ afford new *N*-aryl-*N'*-*p*-nitrophenylcarbimides from the following: *o*-, m.p. 201° , *m*-, m.p. 205° (decomp.), and $p-C_6H_4Me \cdot NH_2$, m.p. 259° ; *m*-xylylidine, m.p. 215° ; $o-NO_2 \cdot C_6H_4 \cdot NH_2$, m.p. 256° ; $o-C_6H_4Cl \cdot NH_2$, m.p. 233° ; $o-C_6H_4Br \cdot NH_2$, m.p. 228° ; *o*-, m.p. 224° , *m*-, m.p. 272° , and $p-C_6H_4I \cdot NH_2$, m.p. 288° ; *o*-, m.p. 212° , and $p-OH \cdot C_6H_4 \cdot NH_2$, m.p. 235° (decomp.); *o*-, m.p. 191° , and $p-OMe \cdot C_6H_4 \cdot NH_2$, m.p. 229° (decomp.); *o*-, m.p. $178-179^\circ$, and $p-OEt \cdot C_6H_4 \cdot NH_2$, m.p. 202° (decomp.); α - $C_{10}H_7 \cdot NH_2$, m.p. 236° ; $p-C_6H_4Ph \cdot NH_2$, m.p. $235-236^\circ$; *o*-, m.p. 186° , *m*-, m.p. $195-196^\circ$, and $p-NH_2 \cdot C_6H_4 \cdot CO_2Et$, m.p. $254-255^\circ$; 2:1:4-, m.p. 260° (decomp.), 3:1:4-, darkens at 245° , chars and decomp. at 260° , 4:1:2-, m.p. $261-262^\circ$, 3:1:2-, m.p. 278° (decomp.), 5:1:2-, m.p. $246-247^\circ$, 4:1:3-, m.p. $263-264^\circ$, and 6:1:3- $NO_2 \cdot C_6H_3Me \cdot NH_2$, m.p. $283-284^\circ$; 1:3:4-, m.p. $209-210^\circ$, 1:5:2-, m.p. 264° , and 1:6:3- $C_6H_3MeCl \cdot NH_2$, m.p. 246° ; 1:3:4-, m.p. $204-205^\circ$, 1:5:2-, m.p. $268-269^\circ$, and 1:6:3- $C_6H_3MeBr \cdot NH_2$, m.p. $248-249^\circ$; 1:5:2-, m.p. 264° , and 1:6:3- $C_6H_3MeI \cdot NH_2$, m.p. 239° ; NH_2Ac , m.p. $295-296^\circ$; NH_2Bz , m.p. 260° ; $NHPhMe$, m.p. 123° ; $NHPhAc$, m.p. $254-255^\circ$; cyclohexylamine, m.p. $169-170^\circ$. M.p. are corr.

A. T. P.

Azides as reagents for the identification of organic compounds. XVIII. *o*-Nitrobenzazide as reagent for identification of phenols. P. P. T. SAH and W. YIN (Rec. trav. chim., 1940, **59**, 238—245; cf. A., 1940, II, 32).—*o*-Nitrobenzhydrazide, m.p. 119° , affords the -azide, decomp. $\sim 44^\circ$, which gives *o*-nitrophenylurethanes (generally of lower m.p. than the *m*- and *p*-isomerides) from the following phenols in ligroin, $NPhMe_2$ being an effective catalyst for the *o*-substituted compounds: $PhOH$, m.p. $96-98^\circ$; *o*-, m.p. $113-114^\circ$, *m*-, m.p. $85-86^\circ$, and *p*-cresol, m.p. $97-98^\circ$; 1:2:4-, m.p. $117-119^\circ$, 1:4:5-, m.p. $90-91^\circ$, and 1:3:4-xylenol, m.p. $99-101^\circ$; *o*-, m.p. 124° , *m*-, m.p. 158° , and $p-NO_2 \cdot C_6H_4 \cdot OH$, m.p. 175° ; *o*-, m.p. $109-110^\circ$, *m*-, m.p. $96-97^\circ$, and $p-C_6H_4Cl \cdot OH$, m.p. $126-127^\circ$; *o*-, m.p. 122° , *m*-, m.p. $91-92^\circ$, and $p-C_6H_4Br \cdot OH$, m.p. $129-130^\circ$; *o*-, m.p. $150-151^\circ$, *m*-, m.p. $98-100^\circ$, and $p-C_6H_4I \cdot OH$, m.p. $133-135^\circ$; 2:4:1- $C_6H_3Cl_2 \cdot OH$, m.p. 123° , and $-C_6H_3Br_2 \cdot OH$, m.p. $121-122^\circ$; 2:4:6:1- $C_6H_3Cl_3 \cdot OH$, m.p. $153-155^\circ$, and $-C_6H_3Br_3 \cdot OH$, m.p. $172-174^\circ$; *o*-, m.p. $136-138^\circ$, *m*-, m.p. $99-100^\circ$, and $p-OMe \cdot C_6H_4 \cdot OH$, m.p. 156° ; α -, m.p. 130° , and β - $C_{10}H_7 \cdot OH$, m.p. 143° . M.p. are corr.

A. T. P.

Determination of phenols by means of benzoic anhydride. A. LEMAN (Bull. Soc. chim., 1940, [v], **7**, 105—113; cf. A., 1939, II, 196).—The sample is heated for 1 hr. at 100° with a solution of Bz_2O in anhyd. C_5H_5N (100 g. in 100 c.c.); H_2O is added and

the heating is continued with frequent shaking for a further hr. after which the mixture is cooled and titrated with N-KOH (phenolphthalein). With coloured samples a spot test on phenolphthalein paper is used. In confirmation the ester is separated from the neutralised solution and washed with H_2O , which is added to the solution; this is then treated with a measured vol. of $\text{N-H}_2\text{SO}_4$ and back-titrated with N-KOH . A blank test is necessary. As with acetylation in $\text{C}_5\text{H}_5\text{N}$, benzoylation of phenols is quantitative and is somewhat more precise but less rapid. Treatment with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$ is almost without effect on phenols or naphthols. In their mixtures with primary alcohols it is therefore possible to determine total OH by Bz_2O and primary alcoholic OH by $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O-C}_5\text{H}_5\text{N}$. Amended m.p. are cited for the following benzoates: Ph, m.p. 69.1° ; o -, m.p. 17° , m -, m.p. 53.6° , and p -, m.p. 70° , -tolyl; p -xylenyl, m.p. 59.5° ; thymyl, m.p. 31.2° ; dibenzoates of o -, m.p. 85.1° and $p\text{-C}_6\text{H}_4(\text{OH})_2$, m.p. 202.5° .

H. W.

Identification of organic compounds. III. Chlorosulphonic acid as a reagent for characterisation of aromatic ethers. E. H. HUNTRESS and F. H. CARTEN (J. Amer. Chem. Soc., 1940, **62**, 603—604).—The following are prepared (method; A., 1940, II, 160). p -Methoxy-, m.p. $110\text{--}111^\circ$, p -ethoxy-, m.p. $149\text{--}150^\circ$, p - n -propoxy-, m.p. $116\text{--}117^\circ$, p - n -butoxy-, m.p. $103\text{--}104^\circ$, 4-methoxy-3-methyl-, m.p. 137° , 4-methoxy-2-methyl-, m.p. $129\text{--}130^\circ$, 2-methoxy-5-methyl-, m.p. 182° , 4-ethoxy-3-methyl-, m.p. $148\text{--}149^\circ$, 4-ethoxy-2-methyl-, m.p. $110\text{--}111^\circ$, 2-ethoxy-5-methyl-, m.p. $138\text{--}138.5^\circ$, 2- n -propoxy-4-methyl-, m.p. $126\text{--}127^\circ$, 4- n -butoxy-5-methyl-, m.p. $95\text{--}96^\circ$, 3:4-, m.p. $135\text{--}136^\circ$, 2:4-, m.p. $166\text{--}167^\circ$, and 2:5-dimethoxy-, m.p. 148° , 3:4-, m.p. $162\text{--}163^\circ$, 2:4-, m.p. $184\text{--}185^\circ$, and 2:5-diethoxy-, m.p. $154\text{--}155^\circ$, 2:3:4-trimethoxy-, m.p. $123\text{--}124^\circ$, 3-chloro-4-methoxy-, m.p. $130\text{--}131^\circ$, 5-chloro-2-methoxy-, m.p. $150\text{--}151^\circ$ (lit. 154°), 3-bromo-4-methoxy-, m.p. $139\text{--}140^\circ$, 5-bromo-2-methoxy-, m.p. $147\text{--}148^\circ$, 5-fluoro-2-methoxy-, m.p. $174\text{--}175^\circ$, 3-chloro-4-ethoxy-, m.p. $132\text{--}133^\circ$, 5-chloro-2-ethoxy-, m.p. $134\text{--}134.5^\circ$, 3-bromo-4-ethoxy-, m.p. $134\text{--}135^\circ$, 5-bromo-2-ethoxy-, m.p. $144\text{--}144.5^\circ$, and p - p' -bromophenoxy-, m.p. $130\text{--}131^\circ$, -benzenesulphonamide; 4-, m.p. $156\text{--}157^\circ$, and 7-methoxy-, m.p. $150\text{--}151^\circ$, 4-, m.p. $164\text{--}165^\circ$, and 7-ethoxy-, m.p. $161\text{--}163^\circ$ (lit. 155°), -naphthalenesulphonamide; Ph_2 ether 4:4'-disulphonamide, m.p. 159° ; $\alpha\beta$ -diphenoxyethane-, m.p. $228\text{--}229^\circ$, and $\alpha\gamma$ -diphenoxypropane-, m.p. $244\text{--}245^\circ$, 4:4'-disulphonamide.

R. S. C.

Potentiometric titration of quinol, p -aminophenol, and p -methylaminophenol with complex chlorides of quadrivalent iridium. S. G. BODANOV and S. E. KRASIKOV (Ann. Sect. Platine, 1939, No. 16, 77—80).—Quinol, $p\text{-NH}_2\text{C}_6\text{H}_4\text{OH}$, and $p\text{-NHMeC}_6\text{H}_4\text{OH}$ are titrated with $0.01\text{N-K}_2\text{IrCl}_6$ or $\text{-(NH}_4)_2\text{IrCl}_6$.

R. T.

Separation and determination of isomeric menthols. R. T. HALL, J. H. HOLCOMB, jun., and D. B. GRIFFIN (Ind. Eng. Chem. [Anal.], 1940, **12**, 187—188).—From a mixture of l -menthol, d -neo-

menthol (I), and d -isomenthol (II), (I) is separated by fractional distillation followed by acetylation and hydrolysis of the recryst. acetate, and (II) by fractional distillation and crystallisation. Total menthol in mixtures is determined by acetylation and determination of the sap. val. of the acetate using KOH in $(\text{CH}_2\text{OH})_2$. Use of $(\text{CH}_2\text{OH})_2$ in place of EtOH greatly reduces the time of saponification.

J. D. R.

Cantharides. I. Titration of cantharidin. B. P. HECHT and L. M. PARKS (J. Amer. Pharm. Assoc., 1940, **29**, 71—77).—Purified cantharidin (I), m.p. $214\text{--}214.5^\circ$ (uncorr.), cannot be titrated quantitatively in presence of EtOH; in this respect, it resembles $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and Bz_2O . Titration of (I) and other anhydrides is effected by adding 0.5N-KOH in EtOH, removing EtOH, and back-titrating with 0.1N-HCl . Cantharidic acid has dissociation const. 5×10^{-9} , whilst the degree of hydrolysis of 0.005M-K cantharidate in H_2O at 25° is 2.28% .

F. O. H.

Diluturates of physiologically important bases. C. E. REDEMANN and C. NIEMANN (J. Amer. Chem. Soc., 1940, **62**, 590—593).—Properties of 5-nitrobarbiturates of 71 org. bases are recorded. The salts of lower aliphatic amines, proteinogenic amines, and some NH_2 -acids are very sparingly sol. and are excellent for quant. separation from some mixtures. The bases are readily recovered by double decomp., which also serves best for formation of the salts. The Mg (0.1 mmol. per l.), Ba, Sr, Ca, Cu, and K (separation from Na) salts are very slightly sol.

R. S. C.

Reactions of diethylbarbituric acid and pyrazolone derivatives with silver proteinate, silver nitrate, and ferric chloride. V. ZANOTTI (Boll. Chim. farm., 1940, **79**, 117—120).—Colour reactions are described.

F. O. H.

Action of a copper-iodine reagent on alkaloids. Precipitation and colour reactions. M. PÉRONNET and J. GUÉNIN (J. Pharm. Chim., 1940, [ix], **1**, 142—147).—Aq. solutions of many alkaloids, but not glucosides or barbiturates, give ppts. when treated with a Cu_2I_2 reagent, which is more sensitive than I-KI. Ppts. obtained with sparteine, quinine, and cocaine contain Cu; they are readily hydrolysed and decompose at 60° . The ppt. obtained with eserine dissolves in aq. NH_3 with violet-red colour. Ephedrine and adrenaline give violet and red colours, respectively.

J. L. D.

Action of heat on hæmoglobin and reversible stages in coagulation of proteins.—See A., 1940, III, 380.

Colour reaction of phenarsazine chloride. J. DELGA (J. Pharm. Chim., 1940, [ix], **1**, 73—76).—Phenarsazine chloride (I) or oxide with the AgNO_3 reagent (10% aq. AgNO_3 : $\text{AcOH} = 1:1$) (5 c.c.) at $100^\circ/10$ min. gives a yellow or orange colour depending on the concn. 0.04 mg. can be detected. Many other As derivatives do not give the reaction. (I) in H_2O (1 in 125,000) is detected similarly.

J. L. D.

A., II.—Organic Chemistry

JULY, 1940

Relative velocity of chloroalkylation of olefines.
—See A., 1940, I, 260.

Grignard syntheses of halogen derivatives of ethylenic alcohols. G. I. SHTUKIN (J. Gen. Chem. Russ., 1940, 10, 77—81).— CH_2AcCl and $\text{CH}_2\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$ in Et_2O at -10° afford α -chloro- β -methyl- Δ^5 -penten- β -ol, b.p. 159° , which with KCN in EtOH gives α -cyano- β -methyl- Δ^5 -penten- β -ol, b.p. $112^\circ/17$ mm. The following are obtained similarly: α -chloro- β -chloromethyl- Δ^5 -penten- β -ol, b.p. $82.5^\circ/14$ mm., from $\text{CO}(\text{CH}_2\text{Cl})_2$, γ -bromo- β -methyl- δ -allyl- Δ^5 -hepten- δ -ol, b.p. 115 — $116^\circ/18$ mm., from $\text{CHPr}^{\text{B}}\text{Br}\cdot\text{CO}_2\text{Et}$, and α -bromo- β -phenyl- Δ^5 -penten- β -ol, decomp. at the b.p., from $\text{COPh}\cdot\text{CH}_2\text{Br}$. R. T.

Preparation of esters in presence of magnesium chloride. P. A. PETIUNIN (J. Gen. Chem. Russ., 1940, 10, 35—38).—Esters are obtained in 60—70% yield from aliphatic acid-alcohol mixtures in presence of anhyd. MgCl_2 (2 hr. at the b.p.). In these conditions BzOH gives only 20—27% yields of ester. R. T.

Direct esterification of higher fatty acids with glycerol. I. Formation of mono- and diglycerides, and their separation. S. KAWAI and H. NOBORI (J. Soc. Chem. Ind. Japan, 1940, 43, 59B).—Esterification was almost complete in 3 hr. with 1 mol. of fatty acid [lauric (I), stearic (II), oleic (III)] to 0.8—1.4 mol. of glycerol at 230 — 240° ; prolonged heating (15—20 hr.) was necessary at 170 — 180° . Glycerides from (I) and (III) were mainly mono- and di- with a small amount of tri-glyceride. Those from (II) were mainly tri- and di- with a small amount of mono-glyceride. Glycerides obtained by prolonged heating at 170 — 180° contained less mono- and di-glyceride than those obtained at 230 — 240° for 3 hr. 85% EtOH was used to separate glycerides of (I) and (II) but 80% EtOH was more effective for those of (III). F. M. F.

Lactic esters: preparation and properties. L. T. SMITH and H. V. CLABORN (Ind. Eng. Chem., 1940, 32, 692—694).—The prep. of lower alkyl lactates (cf. Bogin *et al.*, B., 1934, 637) is improved by using a large excess of alcohol, and removing this and H_2O at low temp. in vac. (column). Na or Ca lactate, the alcohol, and a slight excess of H_2SO_4 are used, for Bu^a to lauryl esters, with C_6H_6 or PhMe to remove H_2O . For higher esters, lactic acid without H_2SO_4 is used. The following are apparently new: iso-amyl, b.p. $82^\circ/7$ mm., n-hexyl, b.p. $75^\circ/2$ mm., β -ethoxy-butyl, b.p. $104^\circ/12$ mm., and -hexyl, b.p. $112^\circ/3.6$ mm., lauryl, b.p. 150 — $153^\circ/4$ mm., and phenylethyl lactate, b.p. $124^\circ/4$ mm. These with keten (cf. A., 1940, II, 5) give n-hexyl, b.p. $135^\circ/17$ mm.,

β -ethyl-butyl, b.p. $127^\circ/14$ mm., and -hexyl, b.p. $145^\circ/13$ mm., lauryl, b.p. $165^\circ/4$ mm., and phenylethyl α -acetoxypionate, b.p. $139^\circ/4$ mm. The prep. of glycol monolactate, b.p. $140^\circ/10$ mm., and of glycerol monolactate, is described. Stearyl lactate has b.p. 180° (decomp.)/2 mm. E. W. W.

Action of sodium alkoxides on ethyl s-diethoxysuccinate. I. Isomerisation of ethyl d-s-diethoxysuccinate into ethyl as-diethoxysuccinate. S. FUKUNAGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, 37, 137—142).—

d - $[\text{CH}(\text{OEt})\cdot\text{CO}_2\text{Et}]_2$, b.p. 156 — $157^\circ/26$ mm., with warm $\text{NaOEt}\cdot\text{EtOH}$ gives Et as-diethoxysuccinate, b.p. 147 — $148^\circ/25$ mm., nearly quantitatively, hydrolysed (warm EtOH-NaOH) to the acid (Ca, + H_2O , and Ba, + H_2O , salts), which when heated (water-bath) alone, or with dil. HCl, or when kept in vac. gives $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. J. L. D.

Determination of dehydroascorbic acid.—See A., 1940, III, 515.

Reaction of ortho-esters with aldehydes. H. W. POST (J. Org. Chem., 1940, 5, 244—249).—Comparative data on the yields of acetals obtained by the interaction of an aldehyde with an aliphatic ortho-ester in presence of a little H_2SO_4 as catalyst show that polymerised aldehydes do not so react. The highest yields are obtained from PhCHO followed by MeCHO and EtCHO. $\text{CH}(\text{OEt})_3$, $\text{CH}(\text{OPh})_3$, and $\text{CH}(\text{OEt})_3$ are decreasingly effective. $\text{CMe}(\text{OEt})_3$ does not behave similarly. Aldehydes such as $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ polymerise under these conditions without perceptible further reaction. MeCHO yields the corresponding dithioacetals with $\text{HCO}\cdot\text{SEt}$ and $\text{HCO}\cdot\text{SPR}$. H. W.

Gattermann synthesis of aldehydes. A. G. MISTRETTA and F. F. NORD (Nature, 1940, 145, 387).—Yields obtained with C_6H_6 , PhMe, PhEt, cumene, etc. as solvents in this synthesis, using AlCl_3 , NaCN, and dry HCl, give an indication of a rule connecting solvent and yield. L. S. T.

Preparation of semicarbazones by functional exchange. B. ANGLA (Ann. Chim. Analyt., 1940, [iii], 22, 10—15).—Semicarbazones are obtained from $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ and the requisite aldehyde or ketone generally in aq. EtOH containing AcOH but frequently in neutral medium if COMe_2 is removed by evaporation or by passage of CO_2 in the cold. The application of the method to the semicarbazones of heptaldehyde, cinnamaldehyde, citronellal, furfuraldehyde, $\text{COMe}\cdot\text{C}_9\text{H}_{19}$, and menthone is described. H. W.

Action of phosphate on hexoses. IV. Formation of lactaldehyde concurrently with acetol.

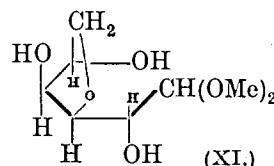
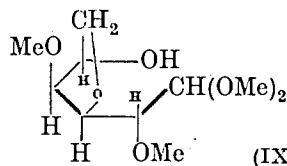
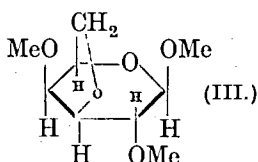
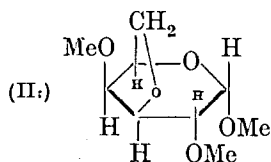
R. Goro (Bull. Chem. Soc. Japan, 1940, 15, 103—106).—In the distillation of acidified K phosphate with glucose (I) (Nodzu *et al.*, A., 1938, II, 172), some $\text{OH}\cdot\text{CHMe}\cdot\text{CHO}$ (II) is formed. The equilibrium $\text{acetol (III)} \rightleftharpoons \text{(II)}$ (shifted to the left, at least in the phosphate system) makes it uncertain whether (II) or (III) is the precursor in the cleavage of (I) to AcCO_2H . E. W. W.

Characterisation of carbohydrates. I. Oxidation of aldoses by hypoiodite in methanol. II. Identification of seven aldomonosaccharides as benziminazole derivatives. S. MOORE and K. P. LINK (J. Biol. Chem., 1940, 133, 293—311).—Aldohexoses and -pentoses are converted into the aldonic acids by I-KOH in MeOH free from COMe_2 but containing a little H_2O at $\sim 40^\circ$. When cold, nearly pure K salts are pptd. in the following yields: from glucose 92, galactose 85, arabinose 83, mannose 30, xylose 8, lyxose and rhamnose 0%. Addition of $\text{BaI}_2\cdot 2\text{H}_2\text{O}$ in MeOH ppts. the residual acid quantitatively as crude Ba salt. These salts are condensed separately with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ by $\text{HCl}\text{--}\text{H}_3\text{PO}_4$ at 135° (with $\text{HCl}\text{--}\text{ZnCl}_2$ at 180° for xylose), giving 60—80% yields of benziminazoles, which, if sol., are pptd. as Cu derivatives and recovered therefrom by H_2S . These in conjunction with their derivatives are better suited than are osazones etc. for characterisation of the sugars. Benziminazoles are reported (if new, the sugar is italicised) from *l*-arabinose, m.p. 235° (decomp.), $[\alpha] +49.5^\circ$ (hydrochloride, m.p. 230° ; picrate, m.p. 158°), *d*-galactose, m.p. 245° (decomp.), $[\alpha] +43.3^\circ$ ($+44.4^\circ$ in HCl) [hydrochloride, m.p. $202\text{--}204^\circ$; picrate, m.p. 217° (decomp.)], *d*-glucose, m.p. 215° , $[\alpha] +9.6^\circ$ ($+9.4^\circ$ in HCl) [hydrochloride, m.p. 180° ; picrate, 203° (decomp.)], *d*-lyxose, m.p. 189° , $[\alpha] -12.8^\circ$ (hydrochloride, m.p. 191° ; picrate, m.p. $95\text{--}99^\circ$), *d*-mannose, m.p. 227° (decomp.), $[\alpha] -22.0^\circ$ [hydrochloride, m.p. $101\text{--}150^\circ$; picrate, m.p. 205° (decomp.)], *l*-rhamnose, m.p. 207° , $[\alpha] +27.4^\circ$ (hydrochloride, m.p. $173\text{--}175^\circ$; picrate, m.p. 168°), and *d*-xylose, m.p. 224° , $[\alpha] +64.8^\circ$ (hydrochloride, m.p. $200\text{--}202^\circ$; picrate, m.p. 191°). $[\alpha]_D^{25}$ in 5% aq. citric acid. Fructose gives only a little of the *d*-arabinose derivative. R. S. C.

Properties of 3:6-anhydrogalactose. W. N. HAWORTH, J. JACKSON, and F. SMITH (J.C.S., 1940, 620—632).—3:6-Anhydromethylgalactopyranosides and their methylation products are prepared. The stable 5-membered anhydro-ring is probably responsible for some of the peculiar properties of 3:6-anhydrogalactose and its derivatives. The 6-*p*-toluenesulphonate, new m.p. 188° , $[\alpha]_D^{25} +118^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (cf. Ohle *et al.*, A., 1933, 492), of α -methyl-

With $\text{MeI}\text{--}\text{Ag}_2\text{O}\text{--}\text{COMe}_2$, (I) gives liquid 2:4-dimethyl-3:6-anhydro- α -methylgalactopyranoside (II), b.p. 90° (bath)/0.01 mm., $[\alpha]_D^{25} +99^\circ$ in Et_2O , which on keeping slowly changes (incompletely) into the β -form (III), m.p. 83° , $[\alpha]_D^{25} -77^\circ$ in H_2O , -87° in CHCl_3 . This $\alpha \rightarrow \beta$ change, also effected by dry HCl , by HBr , by HCl in EtOH or Et_2O (cf. A., 1939, II, 99) or in MeOH , apparently does not involve intermediate formation of a free reducing group. X-Ray examination shows (III), and ebulliometry (II) and (III), to be monomeric. [The enantiomorph of (III) has been obtained by Hands *et al.* (A., 1939, II, 50) and by Percival *et al.* (*ibid.*, 142).] The structure of (III) is established (cf. Percival *et al.*, *loc. cit.*) by its prep. from $\text{Ag}_2\text{O}\text{--}\text{MeI}$ and 3:6-anhydro- β -methylgalactopyranoside (IV), m.p. 119° , $[\alpha]_D^{25} -115^\circ$ in H_2O . (IV) is obtained either (a) by conversion of galactose 6-*p*-toluenesulphonate, through its tetra-acetate, m.p. 107° , $[\alpha]_D +42^\circ$ in CHCl_3 (cf. Ohle *et al.*, *loc. cit.*), into α -acetobromogalactose 6-*p*-toluenesulphonate, m.p. 149° (decomp.), $[\alpha]_D^{25} +165^\circ$ in CHCl_3 , which (Ag_2CO_3) gives β -methylgalactoside 2:3:4-triacetate 6-*p*-toluenesulphonate, $[\alpha]_D^{25} \sim +2.5^\circ$ in CHCl_3 , which gives (Na-MeOH) β -methylgalactopyranoside 6-*p*-toluenesulphonate, m.p. 137° , $[\alpha]_D \sim -3.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, converted by $\text{N-NaOH}\text{--}\text{EtOH}$ into (IV); or (b) from β -methylgalactoside 6-bromohydrin triacetate (Schlubach *et al.*, A., 1932, 369), which with Na-MeOH gives β -methylgalactoside 6-bromohydrin, m.p. ($+ \text{dioxan}$) 106° (sinters at 75°), $[\alpha]_D^{25} +11^\circ$ in H_2O , converted by N-NaOH at 80° into (IV).

With dil. acid, (II) and (III) are easily hydrolysed. With 0.1N- H_2SO_4 at 100° , (II) and (less rapidly) (III) give aldehydo-2:4-dimethyl-3:6-anhydrogalactose (V), m.p. 112° [in one prep. only, from (III)], b.p. 150° (bath)/0.03 mm., $[\alpha]_D^{25} +24^\circ$ in H_2O . (V), which has the usual aldehydic properties, with NH_2Ph in boiling EtOH , gives its anilide, m.p. 123° , $[\alpha]_D^{25} \rightarrow +56^\circ$ in EtOH . Aq. Br oxidises (V) (in the presence of basic PbCO_3 , followed by H_2S and Ag_2O) to 3:6-anhydrogalactonic acid (VI), m.p. 152° , $[\alpha]_D^{25} +66^\circ$ [which with CH_2N_2 yields its Me ester (VII), m.p. 51° , $[\alpha]_D^{25} +67^\circ$ in H_2O (cf. Forbes *et al.*, A., 1940, II, 35)], or (after treatment with Ag_2O and H_2S , and distillation) to a mixture of (VI) and the corresponding lactone (VIII), b.p. $140\text{--}150^\circ$ (bath)/0.01 mm., $[\alpha]_D^{25} +4^\circ$ (const.) in H_2O . Slow evaporation in air of a solution of (VIII) gives (VI) of m.p. 152° , $[\alpha]_D^{25} -66^\circ$ in H_2O . With $\text{MeOH}\text{--}\text{NH}_3$ at -5° , (VII) or (VIII) gives the amide, m.p. 151° , $[\alpha]_D^{25} +81^\circ$ in H_2O . (VI) heated above its m.p. (4 hr.) and distilled gives some



galactopyranoside (*di-p*-toluenesulphonate, m.p. 148° , $[\alpha]_D^{25} +68^\circ$ in $\text{C}_5\text{H}_5\text{N}$) with N-NaOH in EtOH at 60° followed by neutralisation with CO_2 gives 3:6-anhydro- α -methylgalactopyranoside (I) (*loc. cit.*).

(VIII). The stability of the 3:6-anhydro-ring is shown by the prep. of (VI) from (II) and HNO_3 (*d* 1.42) at $50\text{--}80^\circ$.

With excess of 0.5—1% $\text{MeOH}\text{--}\text{HCl}$ at room temp., (II) and (somewhat less readily) (III) both give the relatively strainless 2:4-dimethyl-3:6-anhydrogalact-

ose Me_2 acetal (IX), m.p. 36° , b.p. 95° (bath)/0.02 mm., $[\alpha]_D^{25} +36^\circ$ in H_2O [purified through the *p*-nitrobenzoate (X), b.p. 215° (bath)/0.03 mm.]. With gaseous HCl or HBr, (IX) rapidly yields (III). Similarly, (I) or (IV) with $MeOH-HCl$, followed by Ag_2CO_3 , gives 3 : 6-anhydrogalactose Me_2 acetal (XI), $[\alpha]_D^{25} +36.5^\circ$ in H_2O [2 : 4 : 5-tri-*p*-nitrobenzoate (XII), m.p. 112°]. The open-chain structures are assigned to (IX) and (XI) because of the formation of (X) and (XII), and of the hydrolysis of (IX) and (XI) by 0.1N- H_2SO_4 respectively to (V) and to aldehydo-3 : 6-anhydrogalactose (XIII), a glass, $[\alpha]_D +24^\circ$ in H_2O . This is also obtained from (I) or (IV) and 0.1N- H_2SO_4 . (IX) is directly converted by HCl or HBr in air into (III) with the elimination of 1 Me. Both (IX) and (XI) on methylation (Ag_2O-MeI , $MeOH-HCl$, Ag_2CO_3) give 2 : 4 : 5-trimethyl-3 : 6-anhydrogalactose Me_2 acetal (XIV), b.p. 120° (bath)/0.03 mm., $[\alpha]_D^{25} +41.0^\circ$ in H_2O . Hydrolysis (0.01N- H_2SO_4 at 100°) of (XIV) yields 2 : 4 : 5-trimethylaldehydo-3 : 6-anhydrogalactose (XV), b.p. 105° (bath)/0.02 mm., $[\alpha]_D^{25} +41^\circ$ in H_2O . With aq. Br, (XV) gives 2 : 4 : 5-trimethyl-3 : 6-anhydrogalactonic acid (XVI), $[\alpha]_D^{25} +64^\circ$ (brucine salt, m.p. 114° , $[\alpha]_D \sim -3^\circ$ in H_2O). With $Et_2O-CH_2N_2$, (XVI) gives its *Me* ester, b.p. 115° (bath)/0.03 mm., $[\alpha]_D^{25} +67^\circ$ in H_2O , also obtained by complete methylation of the *Me* ester, b.p. $160-170^\circ$ (bath)/0.03 mm., $[\alpha]_D +38^\circ$ in H_2O , of 3 : 6-anhydrogalactonic acid, $[\alpha]_D^{20} +33^\circ$ in H_2O , prepared by Br oxidation of (XIII).

The above reactions are discussed in relation to the cyclic and dicyclic ring systems involved, and to the stability of these. E. W. W.

Crystalline β' -chloroethyl- β -D-glucoside. J. COMPTON (Contr. Boyce Thompson Inst., 1939, 11, 21-23).— β' -Chloroethyl- β -D-glucoside tetra-acetate (I) (slightly modified prep.; cf. Jackson, A., 1938, II, 174) with $Ba(OMe)_2$ in $MeOH$ for 20 hr. at 5° , followed by the calc. amount of H_2SO_4 , gives (slowly from $EtOAc$) cryst. β' -chloroethyl- β -D-glucoside (II), m.p. $70-71^\circ$, $[\alpha]_D^{25} -29.0^\circ$ in H_2O , reacylated in C_5H_5N to (I). With Raney Ni in $EtOH$ containing aq. NaOH, and H_2 at 3 atm., followed by CO_2 and acetylation of the product, (II) gives ethyl- β -D-glucoside tetra-acetate. E. W. W.

Synthesis of *o*-chlorophenol- β -D-glucoside. L. P. MILLER (Contr. Boyce Thomson Inst., 1939, 11, 25-27).—By the method of Helferich *et al.* (A., 1933, 379), *o*- C_6H_4Cl-OH (I), glucose penta-acetate, and *p*- $C_6H_4Me-SO_3H$ at $115-125^\circ$ give [after removing (I) in H_2O in vac. at $<30^\circ$] the tetra-acetate (II), m.p. $150.5-151^\circ$ (corr.), $[\alpha]_D^{25} -44.6^\circ$ in $CHCl_3$, of *o*-chlorophenol- β -D-glucoside (III), m.p. $171-171.5^\circ$, $[\alpha]_D^{25} -65.3^\circ$ in $EtOH$. $Ba(OMe)_2-MeOH$ converts (II) into (III), which with $Ac_2O-C_5H_5N$ gives (II). Emulsin hydrolyses (III), liberating (I). The product from gladiolus corms (cf. Miller, A., 1938, III, 966) and (I) gives on acetylation a product of m.p. \gg m.p. of (II). E. W. W.

Acetolysis of carrageen mucilage. T. DILLON and P. O'COLLA (Nature, 1940, 145, 749).—Acetylation ($AcOH$ and Ac_2O ; catalyst, SO_2 and Cl_2) of the mucilage and removal of Ac yields two polymeric carbohydrates, $(C_6H_{10}O_5)_n$, probably galactans, one o^* (A., II).

sol. in cold and the other in hot H_2O . The latter gives a wine-red colour with I. L. S. T.

Methylation of chondrosamine hydrochloride. P. A. LEVENE (J. Biol. Chem., 1940, 133, 767).—On methylation of chondrosamine penta-acetate with Me_2SO_4 , the methylpyranoside is formed.

E. M. W.

Amino-acid and peptide esters of choline as possible analogues of the oxytocic hormone of the posterior lobe of the pituitary gland. I. J. M. GULLAND, M. W. PARTRIDGE, and S. S. RANDALL (J.C.S., 1940, 419-425).—Choline chloride (I) and glyceryl chloride hydrochloride in vac. at 100° (4 hr.) give, via the *platinichloride*, m.p. 238° , glycylocholine chloride hydrochloride, m.p. $241-242^\circ$ (cf. Dudley, J.C.S., 1921, 119, 1259) (flavianate, rufianate, and picrolonate). With glycerylglyceryl chloride hydrochloride, (I) similarly gives, via the *picrolonate*, glycerylglycylocholine chloride hydrochloride (+ $3H_2O$), m.p. $128-130^\circ$. $NEt_2[CH_2]_2OBz$ and MeI in C_6H_6 give methyl-diethyl- β -benzoyloxyethylammonium iodide, m.p. 128° (corresponding chloride, m.p. 129°). Lauryl chloride (II) and $NEt_2[CH_2]_2OH$ (III) in $CHCl_3$ give, after washing with $NaHCO_3$, β -diethylaminoethyl laurate, b.p. $194/12$ mm. (hydrochloride, m.p. 109°), which with MeI gives methyl-diethyl- β -lauryloxyethylammonium iodide, m.p. 70° . $NMe_2[CH_2]_2OBz$ (hydrochloride, new m.p. 151°) with MeI gives benzoylcholine iodide, m.p. $243-244^\circ$ (decomp.), converted by $AgCl$ in $EtOH$ into the chloride, new m.p. $206-207^\circ$ (decomp.) (cf. Fourné *et al.*, A., 1914, i, 938). $NMe_2[CH_2]_2OH$ (IV) and (II) give β -dimethylaminoethyl laurate, b.p. $193-194/13$ mm. (hydrochloride, m.p. $143-144^\circ$), which with MeI gives laurylcholine iodide, m.p. $161-162^\circ$ (corresponding chloride, m.p. 54°). This has some oxytocic activity (tested by contraction of the isolated uterus of the virgin guinea-pig) at a dilution of 1/200,000, but larger doses appear to be toxic. PCl_5 and $(S-CH_2-CO_2H)_2$ (V) in Et_2O at $<0^\circ$ give dithioglycollal chloride, an unstable oil, which with (IV) in $CHCl_3$ at 0° forms di-(β -dimethylaminoethyl) dithioglycollate, an oil [also obtained from (IV) and (V) with HCl in $C_2H_2Cl_4$], converted by MeI in C_6H_6 into the dimethiodide (dithioglycollalcholine iodide), $(S-CH_2-CO_2[CH_2]_2NMe_2I)_2$, m.p. $156-157^\circ$. The chloride of carbobenzyloxyglycine (VI) and (III) in $CHCl_3$ give the β -diethylaminoethyl ester (VII) of (VI). The methiodide of (VII) with PH_4I in $AcOH$ with HCl (10 hr.) gives an iodide hydriodide, converted into methyl-diethyl- β -glycyloxyethylammonium dirufanate, m.p. $259-260^\circ$ (decomp.; darkening from $230-235^\circ$). Carbobenzyloxycystinyl chloride (VIII) and (IV) give an oily ester, converted by MeI in C_6H_6 into di-(β -diethylaminoethyl)carbobenzyloxycystine dimethiodide, $[S-CH_2-CH(NH-CO_2CH_2Ph)-CO_2[CH_2]_2NEt_2MeI]_2$ (+ $5H_2O$), deliquescent, m.p. $67-77^\circ$ (evolves gas at $\sim 92^\circ$; chars at 150°). With $OH[CH_2]_2Br$ and C_5H_5N , (VIII) in $CHCl_3$, first at room temp. and then at the b.p. (2 min.), gives β -bromoethylcarbobenzyloxycystine (IX), $[S-CH_2-CH(NH-CO_2CH_2Ph)-CO_2[CH_2]_2Br]_2$, m.p. $86-88^\circ$, which with $NHMe_2$ in C_6H_6 at 60° yields β -dimethylaminoethylcarbobenzyloxycystine (X), an oil,

which forms a *dimethiodide* (carbobenzyloxycystinylcholine iodide) (XI), m.p. 140–142°, also obtained from the β -idoethyl analogue of (IX) with NMe_3 in C_6H_6 [(IX) with NMe_3 gives the *dibromide*, m.p. $\sim 235^\circ$], or, m.p. (+2 H_2O) 70–79° (sinters 64°; chars at 150°), from (IV) and (VIII) in CHCl_3 at 0°, followed by treatment with aq. NH_4HCO_3 , and action of MeI on the resulting (X). PH_4I and (XI) in COMe_2 with HCl at 40° give *cysteylcholine iodide hydriodide* (XII), m.p. 83–85° (decomp.) (sinters 74–75°; chars at 150°), which in EtOH with O_2 forms *cystinylcholine iodide hydriodide* (XIII), a glass. (XII) and (XIII) have slight oxytocic activity. Carbobenzyl-oxyphenylalanyl chloride with (IV) in Et_2O , followed by treatment with NH_4HCO_3 , gives β -dimethylaminoethylcarbobenzyl-oxyphenylalanine, an oil, which with MeI gives the *methiodide* (carbobenzyloxylphenylalanylcholine iodide), m.p. 59–62° (sinters 45–48°; evolves gas at 169°; chars at 190°), which with PH_4I in COMe_2 (under H_2) gives *phenylalanylcholine iodide hydriodide*, m.p. 80–83° (evolving gas) (sinters 40–50°; chars at 200°), which with AgCl forms the *chloride hydrochloride*. Both these are very deliquescent.

E. W. W.

Partial racemisation of glutamic acid in boiling hydrochloric acid solutions. L. E. ARNOW and J. C. OPSAHL (J. Biol. Chem., 1940, **133**, 765–766).—The extent of racemisation of *l*(+)-glutamic acid caused by boiling HCl is sufficient to account for the results of Johnson (A., 1940, III, 424) but not those of Kögl *et al.* (A., 1939, III, 489).

E. M. W.

Preparation of *d*(–)-glutamic acid from *dl*-glutamic acid by enzymic resolution. J. S. FRUTON, G. W. IRVING, jun., and M. BERGMANN (J. Biol. Chem., 1940, **133**, 703–705).—By the action of NH_2Ph on carbobenzyloxy-*dl*-glutamic acid in the presence of papain–cysteine, only the *l*- NH_2 -acid forms an anilide. Pure *d*(–)-glutamic acid can be obtained from the filtrate by hydrogenation and recrystallisation of the hydrochloride.

E. M. W.

Reactions of some high-mol. wt. fatty acid derivatives. M. R. McCORKLE (Iowa State Coll. J. Sci., 1939, **14**, 64–66).—For thioamides cf. Ralston *et al.* (A., 1939, II, 204). β -Imino- α -*n*-decylmyristonitrile, b.p. 230–235°/3 mm. (from lauronitrile and NPhEtLi), is hydrolysed by EtOH-HCl to β -keto- α -*n*-decylmyristonitrile, m.p. 44–45°, and by conc. H_2SO_4 to β -keto- α -*n*-decylmyristamide, m.p. 114–115°, which yields laurone with EtOH-KOH . Similarly stearonitrile yields β -imino-, m.p. 54–55°, and β -keto- α -*n*-hexadecylarachidonitrile, m.p. 68–69°, and β -keto- α -*n*-hexadecylarachidonamide, m.p. 114–115°, hydrolysed to stearone. Fries rearrangement of *p*-diphenyllyl stearate, m.p. 73–74°, yields 2-hydroxy-5-phenyl-, m.p. 63–64° [*Me ether* (also prepared from 2 : 5 : 1- $\text{OMe-C}_6\text{H}_4\text{Ph-MgBr}$ and stearonitrile), m.p. 53–54°], and *p*-*p'*-hydroxyphenyl-stearophenone, m.p. 141–142°, the *Me ether*, m.p. 116–117° (also prepared from p - $\text{C}_6\text{H}_4\text{Ph-OMe}$, stearyl chloride, and AlCl_3), of which is oxidised to p - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Stearonitrile yields with β - $\text{C}_{10}\text{H}_7\text{-MgBr}$, β -stearoylnaphthalene, m.p. 65–66°, with p - $\text{C}_6\text{H}_4\text{PhLi}$, *p*-phenylstearophenone (I), m.p. 108–109°, and with MgMeBr , β -keto-*n*-nonacosane, m.p. 55–56°. Stearyl chloride with Ph_2O and with

Ph_2O yields (I) and *p*-phenoxystearophenone (II), m.p. 62–63°, respectively. Sulphonation of (I) yields 4-sulpho-4'-stearoyldiphenyl, m.p. 142–145°, oxidised to 4-sulphodiphenyl-4'-carboxylic acid (*p*-toluidine salt, m.p. 288–289°) (also obtained by sulphonating p - $\text{C}_6\text{H}_4\text{Ph-CO}_2\text{H}$), which on fusion with KOH yields 4 : 4'- $\text{OH-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$. (I) with ClSO_3H yields a trisulphonic acid, oxidised to 4 : 4'- $\text{SO}_3\text{H-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$. Sulphonation of (II) yields *p*-*p'*-stearoyl-, m.p. 95–98°, oxidised (dil. HNO_3) to *p*-*p'*-carboxy-phenoxystearophenone (*p*-toluidine salt, m.p. 266–267°), which on fusion with KOH gives p - $\text{OH-C}_6\text{H}_4\text{-CO}_2\text{H}$. Hydrogenation (Adkin's $\text{Cu-Cr}_2\text{O}_3$ catalyst) of lauro- and stearo-nitriles yields *di*-*n*-dodecyl-, m.p. 52–53°, and *octadecyl-amine*, m.p. 73–74°, respectively, which when heated with the corresponding chlorides (from the alcohols and SOCl_2) yield *tri*-*n*-dodecyl- (hydrochloride, m.p. 78–79°) and *octadecyl-amine*, m.p. 54–55° (hydrochloride, m.p. 96–97°). Laurone and stearone are prepared by heating the acids with Fe powder. Reduction ($\text{Na} + \text{BuOH}$) of myristone and stearone yields $(\text{C}_{13}\text{H}_{27})_2\text{CH-OH}$ and $(\text{C}_{17}\text{H}_{35})_2\text{CH-OH}$. Attempts to synthesise $[(\text{C}_{17}\text{H}_{35})_2\text{CH}]_2$ from σ -iodopentatriacontane, m.p. 43.5–45°, failed, but reduction of the latter yields *n*- $\text{C}_{35}\text{H}_{72}$. *n*-Octadecanol with $\text{HBr-conc. H}_2\text{SO}_4$ gives the bromide (87%). $\text{C}_{12}\text{H}_{25}\text{-MgBr}$ with CuCl_2 gives 22% of *n*- $\text{C}_{24}\text{H}_{50}$, and with laurone yields μ -*n*-dodecyltricosan- μ -ol, b.p. 270–275°/2 mm. $\text{C}_{18}\text{H}_{37}\text{-MgBr}$ (or the chloride, prepared in 64% yield) with stearone yields σ -*n*-octadecylpentatriacontan- σ -ol (III), m.p. 58–59°. The *iodide*, m.p. 29–32°, from (III) with Na gives an unsaturated mixture, m.p. 40–42°, and is reduced ($\text{Zn} + \text{HCl}$ in AcOH) to σ -*n*-octadecylpentatriacontane, m.p. 45–46°. Dehydration (p - $\text{C}_6\text{H}_4\text{Me-SO}_3\text{H}$) of (III) gives a mixture of olefines, m.p. 42–44°. The prep. and reactions of these compounds showed no differences from lower members of the series.

A. LI.

Structure of additive products of metal halides and unsaturated compounds. R. C. FREIDLIN and A. N. NESMEJANOV (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 60–64).— $\text{Hg}(\text{C}_2\text{H}_2)_2\text{Cl}_2$ (I) (from HgCl_2 and C_2H_2 in dil. HCl) or $\text{Hg}(\text{C}_2\text{H}_2)_2\text{Cl}_2$ (II) [from (I) and NH_3 in CHCl_3] yields with SnPh_2Cl_2 , in neutral solution, HgPhCl , and in alkaline solution, HgPh_2 , with CH_3N_2 , $\text{Hg}(\text{CH}_2\text{Cl})\text{Cl}$, and with PPh_3 , $\text{Hg}(\text{PPh}_3)_2\text{Cl}_2$, C_2H_2 being eliminated in each case, but with I in Et_2O , CHCl:CHI and HgClI are obtained. From these reactions and spectroscopic evidence it is suggested that (I) and (II) are resonance hybrids $\text{CHCl:CH-HgCl} \longleftrightarrow \text{Hg}(\text{C}_2\text{H}_2)_2\text{Cl}_2$ and $(\text{CHCl:CH})_2\text{Hg} \longleftrightarrow \text{Hg}(\text{C}_2\text{H}_2)_2\text{Cl}_2$.

A. LI.

Action of organomagnesium compounds on trialkoxychlorosilanes. M. N. KALININ (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 365–369).— SiCl_4 with EtOH , $\text{Bu}^\text{t}\text{OH}$, and *iso*- $\text{C}_5\text{H}_{11}\text{-OH}$ in C_6H_6 at 0°, then at 50–60°, yields respectively $\text{SiCl}(\text{OEt})_3$, chlorotri-isobutoxy-, b.p. 229–231°, and *iso*amylorxy-silane, b.p. 143–146°/12 mm. With MgEtBr and MgPhBr these yield respectively tri-ethoxy-, *iso*-butoxy-, b.p. 101–103°/8 mm., and *iso*amylorxy-ethylsilane, b.p. 151–154°/17 mm., and tri-ethoxy-, *iso*-butoxy-, b.p. 154–157°/10 mm., and *iso*amylorxy-

phenylsilane, b.p. 194—197°/18 mm. The physical properties of these compounds are tabulated.

A. Li.

Application of Meyer's reaction to lead. M. LESBRE (Compt. rend., 1940, **210**, 535—536; cf. A., 1935, 611).—RI (R = Me, Et, Pr^a, Pr^β, Bu^a, CH₂Ph, allyl) reacts slowly with a solution of 3PbO·H₂O in aq. NaOH (0.15 g.-mol. of Pb. per l.), giving the *alkyl-plumbonic acid*, R₃Pb(OH)₃ or R₃PbO₂H (I); traces of I catalyse the reaction. (I) is pptd. from the acidified solution by addition of aq. NH₃, and purified by reprecipitation from HBr solution with dil. KOH. The (I) are sol. in dil. acids and conc. alkalis, but insol. in aq. NH₃ and dil. alkalis; pyrolysis in a sealed tube gives PbO, H₂O, and ROH, CH₂Ph·Pb(OH)₃ also affording Pb(CH₂Ph)₄. The metallic plumbonates are very unstable and readily hydrolysed.

A. J. E. W.

Hydroxylamine-thiocarbamide platinum compounds.—See A., 1940, I, 267.

Dehydrogenation and irreversible catalysis of 1-vinyl-Δ³-cyclohexene. S. R. SERGIENKO (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 73—75; cf. A., 1939, II, 205).—With Cr₂O₃ at 400°, 1-vinyl-Δ³-cyclohexene (I) yields PhEt (99%) with a trace of styrene. Pd-C, but not Pt-black, catalyses the irreversible reaction: (I) (3 mols.) → 2PhEt + C₆H₁₁Et.

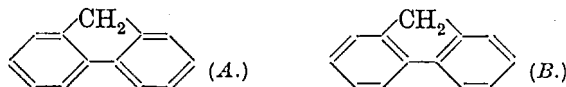
A. Li.

Fluorescence and oxidation in conjugated ring systems. J. WEISS (Nature, 1940, **145**, 744—745).—The essential conditions in these systems for fluorescence, which is due to highly mobile electrons, and the analogy to a metal of the structure and chemical reactivity of conjugated ring systems are discussed. The structures of hydrocarbon peroxides and of graphitic oxide are considered, and a mechanism for the action of carcinogenic hydrocarbons is suggested.

L. S. T.

Structure of aromatic compounds. II. N. CAMPBELL, W. ANDERSON, and J. GILMORE (J.C.S., 1940, 446—451; cf. A., 1937, II, 407).—Polycyclic aromatic compounds are considered as resonance hybrids, the properties of which are explained by the non-equivalence of C—C linkings. This accounts for previous results (cf. also Lindner *et al.*, A., 1939, II, 448; Sandin *et al.*, *ibid.*, 541). As before, the halogen reactivity is measured by the piperidine method (Le Fèvre *et al.*, A., 1927, 653). The reactivity of 9-bromo-10-nitrophenanthrene and the non-reactivity of 3-bromo-4-nitroacenaphthene agree with the view that reactivity depends on a C:C or conjugated system. *o*-, *m*-, and *p*-C₆H₄Cl·CHO and MeNO₂ with aq. NaOH give *o*- (I), m.p. 47°, *m*- (II), m.p. 48—49°, and *p*-chloro-*o*-nitrostyrene (III), m.p. 113—114°. *o*-C₆H₄Br·CHO (IV) (2 : 4-dinitrophenylhydrazones, m.p. 199—200°) with MeNO₂ gives *o*-bromo-*o*-nitrostyrene (V), m.p. 86°. Of (I)—(III) and (V), only (II) is non-reactive. Attempts to prepare 2 : 1- and 4 : 1-C₆H₄Br·C(NO₂)₂·CHPh were unsuccessful. CH₂Ph·NO₂, NH₂Me, HCl, Na₂CO₃, EtOH, and (IV) when heated give a *diphenyl-o-bromophenylisooxazole*, m.p. 135°; *p*-C₆H₄Br·CHO similarly gives an *isomeride*, m.p. 175° (180° after sublimation). The prep. of 1 : 4-C₆H₄Ph·NO₂ is improved. 3 : 1 : 4-NO₂·C₆H₃Ph·NH₂

yields 4-bromo-3-nitrodiphenyl, m.p. 41—42°. 1 : 5 : 2-C₆H₃PhBr·NH₂ yields 5-bromo-2-nitrodiphenyl (?), m.p. 230°. The non-reactivity of 2-bromo-4'-, 4-bromo-4'', and 4-bromo-2'-nitrodiphenyl, and of 2-bromo-7-nitrofluorene shows that the influence of NO₂ is not transmitted from one ring to another. The slight reactivity of 4-bromo-5-nitrohydrindene, new m.p. ~20°, is confirmed. Reactivity of derivatives of fluorene (VI) suggests that (VI) has the structure (A), but it is probably a resonance hybrid of (A) and (B).



3-Nitro-2-amino- yields 2-bromo-3-nitro-fluorene, m.p. 120—121°. Attempts to prepare 1 : 2-substituted derivatives of (VI) are unsuccessful. 7-Bromo-2-aminofluorene (VII) with *p*-C₆H₄Me·SO₂Cl (VIII) and C₅H₅N yields 7-bromo-, m.p. 211°, which with Br·CHCl₃ gives 3 : 7-dibromo-2-*p*-toluenesulphonamido-fluorene (IX), m.p. 203°. 2-Amino- also yields 2-*p*-toluenesulphonamido-fluorene, m.p. 157—158°, which is brominated to (IX). On hydrolysis, (IX) gives 3 : 7-dibromo-2-aminofluorene, m.p. 135°, from which 3 : 7-dibromofluorene, m.p. 129°, is obtained. This is oxidised by Na₂Cr₂O₇-AcOH to 3 : 7-dibromofluorenone, m.p. 200°. With Ac₂O in boiling C₁₀H₁₂, (VII) gives its *Ac* derivative, m.p. 229—231°, brominated to 3 : 7-dibromo-2-acetamidofluorene, m.p. 272°. The pronounced reactivity of 3-bromo-2-nitroacenaphthene suggests that the acenaphthene nucleus has a resonance structure like that of C₁₀H₈. 1-Nitro- with boiling AcOH·Br gives 4(?)-bromo-1-nitro-acenaphthene, m.p. 157°. Presence of Me decreases the reactivity of bromonitrotoluenes. 1 : 3 : 4-C₆H₃MeBr·NH₂ yields 3-bromo-4-nitrotoluene, m.p. 36—37°. Bromination of 1 : 4 : 2' : 1'-C₆H₃Me·SO₂·NH·C₆H₄Me (in an attempt to obtain 1 : 3 : 2-C₆H₃MeBr·NO₂) gives 5-bromo-2-*p*-toluenesulphonamidotoluene, m.p. 136°, also obtained from (VIII) and 1 : 5 : 2-C₆H₃MeBr·NH₂. E. W. W.

Isomerisation accompanying alkylation. II. Alkylation of benzene with olefines, naphthenes, alcohols, and alkyl halides. V. N. IPATIEV, H. PINES, and L. SCHMERLING (J. Org. Chem., 1940, **5**, 253—263; cf. A., 1938, II, 130).—The alkylation of C₆H₆ with olefines, alcohols, and naphthenes in the presence of H₂SO₄ leads to the formation of alkylbenzenes different from those obtained when the reactions are catalysed by AlCl₃. In presence of H₂SO₄, Δ^a-pentene gives a mixture of β- and γ-phenylpentane, and CH₂:CHPr^β affords *tert*-amylbenzene. Isomerisation does not occur in presence of AlCl₃; CH₂:CHPr^β gives CHPhMePr^β. Pr^aOH and C₆H₆ give PhPr^β in presence of H₂SO₄ and PhPr^a in presence of AlCl₃. *cyclo*Propane (I) gives exclusively PhPr^a in presence of AlCl₃ but H₂SO₄ induces isomerisation if the temp. is sufficiently high; thus at 65° (I) and C₆H₆ afford PhPr^β. Alkyl halides with C₆H₆ and AlCl₃ give a mixture of isomerides; even at 35° much PhPr^a results from Pr^aCl and C₆H₆. The mechanism of the alkylations is discussed. H. W.

Association of the nitrotoluenes. W. HÜCKEL and M. VON SCHALSCHA-EHRENFELD (J. pr. Chem.,

1940, [ii], 154, 57—65).—The apparent mol. wts. (M) of *o*-, *m*-, and *p*-nitrotoluenes, $1\text{-C}_{10}\text{H}_7\text{NO}_2$, *trans*- β -decalol (I), and α -fenchol (II) have been determined cryoscopically and ebullioscopically in C_6H_6 and in cyclohexane (III). For the nitrotoluenes, M increases almost equally with increasing concn., but the increase in C_6H_6 is \gg in (III). It is inferred that the dipole moments do not determine the degree of association of these compounds. (II) shows similar association to isoborneol, the M increasing with increasing concn. in both solvents, whereas the M of (I) increases with increasing concn. in (III) but not in C_6H_6 . J. W. S.

Catalytic dehydrogenation of ethylbenzene. S. R. SERGIENKO (Compt. rend. Acad. Sci. U.R.S.S., 1940, 26, 69—72; cf. A., 1939, II, 205).—The dehydrogenation (Cr_2O_3) of PhEt to styrene begins at 425° , reaching 25—30% at 525° . At 525° some 1-ethylphenanthrene and PhMe are formed. A. Li.

Friedel and Crafts reaction. II. Condensation of *o*- and *m*-dichlorobenzene with chloroform and carbon tetrachloride. S. D. WILSON and Y. Y. CHENG (J. Org. Chem., 1940, 5, 223—226; cf. A., 1936, 976).— AlCl_3 is added to a mixture of CHCl_3 and *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ and the mixture is heated at $55\text{--}60^\circ$ for 8 hr., thereby giving (probably) 3:4:3':4':3'':4''-hexachlorotriphenylmethane, m.p. $160\text{--}5\text{--}162^\circ$, in 15% yield. Similarly *m*- $\text{C}_6\text{H}_4\text{Cl}_2$ at $60\text{--}65^\circ$ for 12—14 hr. affords 2:4:2':4':2'':4''-hexachlorotriphenylmethane, m.p. $227\text{--}228\text{--}5^\circ$, in 18% yield. CCl_4 and *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ give (probably) 3:4:3':4'-tetrachlorobenzophenone chloride, hydrolysed by hot, 95% EtOH to 3:4:3':4'-tetrachlorobenzophenone, m.p. $141\text{--}142^\circ$. 2:4:2':4'-Tetrachlorobenzophenone dichloride, m.p. $139\text{--}140\text{--}5^\circ$, is derived in 60% yield from *m*- $\text{C}_6\text{H}_4\text{Cl}_2$. H. W.

Organic selenium derivatives. V. Reaction products of selenium in [aqueous] sodium sulphide with benzyl derivatives. G. SPERONI and G. MANNELLI (Gazzetta, 1940, 70, 246—253).—Se in conc. Na_2S with $\text{C}_6\text{H}_5\text{X}\cdot\text{CH}_2\text{Cl}$ gives a product (cf. A., 1940, II, 160) which is a solid solution of a disulphide in a diselenide (cf. Fromm *et al.*, A., 1913, i, 1323), as is shown by comparing the m.p. with that of mixtures of these. Products from CH_2PhCl , *m*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$, and *o*- (I) and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$ (II) are examined. With Se in aq. Na_2Se , (I) and (II) give respectively *di*-*o*-, m.p. $105\text{--}5^\circ$, and *di*-*p*-chlorobenzyl diselenide, m.p. 82° . *Di*-*p*-bromobenzyl diselenide, m.p. 106° , is prepared similarly. With Na_2Se in COMe_2 , *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ gives *di*-*o*-nitrobenzyl diselenide, m.p. $103\text{--}5^\circ$. K_2SSeO_3 and 5:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}_2\text{Cl}$ (III) give *K* 2-chloro-5-nitrobenzylseleniosulphate. This with I-KI , or on heating with dil. HCl , gives *di*-2-chloro-5-nitrobenzyl diselenide, m.p. $171\text{--}5^\circ$, also obtained from (III) and aq. Na_2Se . E. W. W.

Synthesis of dialkylphenanthrenes. 3:5-Dimethyl-, 5-methyl-2-ethyl-, and 5-methyl-3-ethyl-phenanthrene. Abnormal selenium dehydrogenation of strophanthidin. E. E. LEWIS and R. C. ELDERFIELD (J. Org. Chem., 1940, 5, 290—299).—If strophanthidin and Se are heated very

rapidly in N_2 at 340° and then kept at $340\text{--}360^\circ$ for 32 hr. small amounts of a hydrocarbon (I), $\text{C}_{17}\text{H}_{16}$ or $\text{C}_{16}\text{H}_{14}$, m.p. $131\text{--}132^\circ$, are obtained, not identical with the product of Elderfield *et al.* (A., 1934, 657, 1359). (I) gives a picrate, m.p. $142\text{--}144^\circ$, an additive compound, m.p. $168\text{--}5\text{--}170\text{--}5^\circ$, with *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$, and a quinone, $\text{C}_{17}\text{H}_{14}\text{O}_2$ or $\text{C}_{16}\text{H}_{12}\text{O}_2$, m.p. $207\text{--}208^\circ$. *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$, 2:3:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHO}$, and Ac_2O at $105\text{--}110^\circ$ yield 2-nitro-3-methyl- α -*p*-tolylcinnamic acid, m.p. $250\text{--}5\text{--}251\text{--}5^\circ$, reduced ($\text{FeSO}_4\text{-aq. NH}_3$) to the 2- NH_2 -compound, m.p. $176\text{--}5\text{--}177\text{--}5^\circ$; this is transformed by diazotisation and treatment with $\text{Na}_2\text{S}_2\text{O}_4$ into 3:5-dimethyl-10-phenanthroic acid, m.p. $216\text{--}217^\circ$, which is decarboxylated (basic Cu carbonate in quinoline at $240\text{--}260^\circ$) to 3:5-dimethylphenanthrene (II), m.p. $53\text{--}5\text{--}54\text{--}5^\circ$ (picrate, m.p. $139\text{--}139\text{--}5^\circ$; styphnate, m.p. $124\text{--}125^\circ$; 3:5-dimethylphenanthraquinone, m.p. $124\text{--}5\text{--}125\text{--}5^\circ$, and the corresponding quinoxaline, $\text{C}_{22}\text{H}_{16}\text{N}_2$, m.p. $173\text{--}173\text{--}5^\circ$). *m*-Allyl-ethylbenzene, b.p. $88^\circ/18\text{ mm.}$, from *m*- $\text{C}_6\text{H}_4\text{BrEt}$ and $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Br}$, is oxidised (cold, dil. KMnO_4) to *m*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. $62\text{--}63^\circ$, which is condensed with 2:3:6- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHO}$ to 2-nitro- α -*m*-ethylphenyl-3-methylcinnamic acid, m.p. $144\text{--}5\text{--}145\text{--}5^\circ$. The corresponding NH_2 -acid is cyclised to 5-methyl-2-ethyl-10-phenanthroic acid, m.p. $171\text{--}5\text{--}172\text{--}5^\circ$, which gives 5-methyl-2-ethylphenanthrene (III) [additive compounds, m.p. $111\text{--}112^\circ$ and $49\text{--}50^\circ$ respectively with *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ and 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$; unstable picrate, m.p. $101\text{--}102^\circ$], from which a cryst. quinone or quinoxaline could not be derived. *p*- $\text{C}_6\text{H}_4\text{EtBr}$, b.p. $86\text{--}88^\circ/15\text{ mm.}$, is converted into *p*-allyl-ethylbenzene, b.p. $94\text{--}95^\circ/23\text{ mm.}$, and thence into *p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. $88\text{--}89^\circ$. This gives 2-nitro-, m.p. $182\text{--}5\text{--}184\text{--}5^\circ$, 2-amino-, m.p. $167\text{--}168^\circ$, α -*p*'-ethylphenyl-3-methylcinnamic acid and 5-methyl-3-ethyl-10-phenanthroic acid, m.p. $186\text{--}187^\circ$, which is decarboxylated to 5-methyl-3-ethylphenanthrene (IV) [additive compounds, m.p. $124\text{--}125^\circ$ and $74\text{--}76^\circ$, with *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ and 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$; picrate, m.p. 111°]. (I) is not identical with (II), (III), or (IV). The prep. of 2-bromo-5-methyl-, m.p. $122\text{--}123^\circ$, and 3-bromo-6-methyl-, m.p. $93\text{--}5\text{--}94\text{--}5^\circ$, -phenylacetic acid is described. The latter acid is transformed into 2-nitro- α -2'-bromo-5'-methylphenyl-3-methylcinnamic acid, m.p. $190\text{--}191^\circ$, reduced to the 2- NH_2 -acid, which could not be satisfactorily cyclised. H. W.

Preparation of cholesterol and various cholestadienes. R. L. VAN PEURSEM (Iowa State Coll. J. Sci., 1939, 14, 101—102).—The properties of cholesterol and $\Delta^3\text{:}^5$ -cholestadiene are described again (cf. A., 1939, II, 105). Either of these with Cr_2O_3 yields Δ^4 -cholestene-3:6-dione (identified as monophenyldiazone). $\Delta^4\text{:}^6$ -Cholestadiene differs from 7-dehydrocholestene isomeride (Eck *et al.*, *ibid.*, 539). A. Li.

Derivatives of naphthyl- and tetrahydronaphthyl-oxamic acids, and preparation of 4-nitro- α -naphthylamine. S. I. SERGIEVSKAJA (J. Gen. Chem. Russ., 1940, 10, 55—64).— $\text{NHPh}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ and HNO_3 (*d* 1.53) yield *Et* 2:4-dinitro-oxanilate, m.p. $142\text{--}143^\circ$. *Et* α -naphthyl-

oxamate (I) and HNO_3 (d 1.4) (1 hr. at 15–20°) afford *Et* 4-nitro- α -naphthylloxamate, m.p. 158–159°, converted by heating at 70° with 10% NaOH into 4:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$; some 2- NO_2 -derivative is also formed in this reaction. (I) and Br in $\text{C}_2\text{H}_4\text{Cl}_2$ (1.5 hr. at room temp.) yield *Et* 4-bromo- α -naphthylloxamate, m.p. 135–136°, which gives 4-bromo- α -naphthylloxamic acid, m.p. 180° (decomp.), with boiling 10% NaOH, and 4:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}_2$ with boiling 60% KOH. The following are prepared analogously: 1-bromo- β -naphthylloxamic acid, m.p. 156–157° (*Et* ester, m.p. 97°), and *Et* 1-nitro- β -naphthylloxamate, m.p. 135–137° (small amounts of 6- and 8- NO_2 -derivatives, not isolated, are produced simultaneously). 5:6:7:8-Tetrahydro- α -naphthylamine and $\text{Et}_2\text{C}_2\text{O}_4$ (4 hr. at the b.p.) yield *Et* 5:6:7:8-tetrahydro- α -naphthylloxamate (II), m.p. 83.5–84°, together with *di*-(5:6:7:8-tetrahydro- α -naphthyl)oxamide, m.p. 258°. (II) is hydrolysed (10% NaOH at 100°) to 5:6:7:8-tetrahydro- α -naphthylloxamic acid, m.p. 156–157° [*amide*, m.p. 218–219°; 4-Br-derivative, m.p. 180–181° (decomp.) (*Et* ester, m.p. 135–136°); 4- NO_2 -derivative, m.p. 163–164°]. 5:6:7:8-Tetrahydro- β -naphthylloxamic acid, m.p. 158° (decomp.) (*Et* ester, m.p. 81–82°; *amide*, m.p. 198–199°), is prepared analogously. R. T.

Derivatives of sulphonamides.—See B., 1940, 494.

N⁴ - Diethylaminoalkyl - N¹ - dialkylsulphanil amides [p-diethylaminoalkylaminobenzenesulphonodialkylamides] and related compounds. J. WALKER (J.C.S., 1940, 686–692).—

$p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ (I) and $\text{NHMe}_2\text{-COMe}_2\text{-Et}_2\text{O}$ give $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NMe}_2$ (II), new m.p. 145–146° (solvated from aq. EtOH, m.p. 106–107°) (cf. Ganapati, A., 1939, II, 107), hydrolysed to $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NMe}_2$ (III), new m.p. 169–170°. (II) and K in xylene at 140–150° (bath) give a K derivative, converted by $\text{NEt}_2\cdot[\text{CH}_2]_2\text{Cl}$ into an oil, b.p. ~195°/0.05 mm., and $p\text{-N-}\beta\text{-diethylaminoethylacetamidobenzenesulphonodimethylamide}$, b.p. 210°/0.05 mm., hydrolysed by 16% HCl to $p\text{-}\beta\text{-diethylaminomethylaminobenzenesulphonodimethylamide}$, b.p. 195°/0.08 mm. (*hydrochloride*, m.p. 159–160°), also obtained in small yield from (III) and $\text{NEt}_2\cdot[\text{CH}_2]_2\text{Cl}\cdot\text{HCl}$ at 145–150°. (I) and piperidine in COMe_2 afford $p\text{-acetamidobenzenesulphonopiperidine}$, new m.p. 149–150°, converted through the K salt into the Ac derivative of $p\text{-}\beta\text{-diethylaminoethylaminobenzenesulphonopiperidine}$ (*hydrochloride*, m.p. 201–203°). $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NEt}_2$ (IV) (a gum from the monohydrate at 100°) is converted as above into $p\text{-NEt}_2\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NEt}_2$ (*hydrochloride*, m.p. 138–139°) and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NEt}_2\cdot\text{NEt}_2\cdot[\text{CH}_2]_2\text{Cl}$ and (IV) similarly afford $p\text{-NEt}_2\cdot[\text{CH}_2]_3\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NEt}_2$ (*dihydrochloride*, m.p. 180–181°). NACPhEt or $\text{HCO}\cdot\text{NPhEt}$ and ClSO_3H , followed by aq. NH_3 , give $p\text{-N-acetyl-}$, m.p. 126–127° (+ H_2O , lost at ~102°) (low yield), or $p\text{-N-formyl-ethylaminobenzenesulphonamide}$, m.p. 188–189° (64% yield), respectively. The latter is hydrolysed by 16% HCl to $p\text{-ethylaminobenzenesulphonamide}$, m.p. 134–135.5°. (I) and $\text{NH}_2\text{Et}\cdot\text{COMe}_2\text{-Et}_2\text{O}$ afford $p\text{-acetamidobenzenesulphonethyl-}$

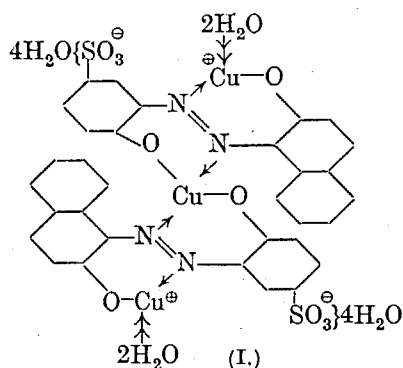
amide, m.p. 153–155°, less readily obtained (impure) from $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and 95% $\text{EtOH}\cdot\text{KOH}\cdot\text{EtI}$. $\text{HCO}\cdot\text{NNApH}$ and $\text{NEt}_2\cdot[\text{CH}_2]_2\text{Cl}$ in C_6H_6 give $N\text{-}\beta\text{-diethylaminoethylformanilide}$ (V), b.p. 143–144°/0.1 mm., converted by 22% HCl into $N\text{-}\beta\text{-diethylaminoethylaniline}$, b.p. 152–153°/18 mm. [Ac derivative (VI), b.p. 118–120°/0.1 mm.]. (V) or (VI) is unchanged by ClSO_3H . $\text{HCO}\cdot\text{NNApH}$ and $\gamma\text{-bromopropylphthahmide}$ at 100° (bath) afford $N\text{-}\gamma\text{-phthalimidopropylformanilide}$, m.p. 126°, converted by ClSO_3H into $N\text{-}\gamma\text{-(o-carboxybenzamido)propylaniline}$ (?) *p-sulphonic acid*, m.p. 250–253°. 2-Acetamidonaphthalene-6-sulphonamide, m.p. 246–247° (intermediate chloride best obtained from 2:6- $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$ and ClSO_3H), is hydrolysed by 16% HCl to the 2- NH_2 -derivative, m.p. 233.5–235°. Antimalarial tests are recorded. Some of the above compounds are inactive in *Pl. relictum* infection of canaries. A. T. P.

Chemotherapy of bacterial infections. II. Synthesis of sulphanilamide derivatives and relation of chemical constitution to chemotherapeutic action. K. GANAPATHI (Proc. Indian Acad. Sci., 1940, 11, A, 298–311).— $p\text{-Vanillylideneaminobenzenesulphonamide}$, m.p. 198–199° [from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (I) and vanillin in EtOH], is reduced by $\text{Zn}\cdot\text{AcOH}$ to $p\text{-4'-hydroxy-3'-methoxybenzylaminobenzenesulphonamide}$, m.p. 167°. Phenylalanine and $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ (II) in 2.5N-NaOH afford, after hydrolysis (dil. HCl) of the Ac derivative, m.p. 205–206°, $N\text{-sulphanilylphenylalanine}$, m.p. 196–197° (decomp.). *dl*-Taurine affords $N\text{-sulphanilyltaurine}$. 1:3:6- or 2:5:7- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$ gives 1-sulphanilamidonaphthalene-3:6- or 2-sulphanilamidonaphthalene-5:7-disulphonic acid, respectively. 1- and 2-Sulphanilamido-8-naphthol-3:6-disulphonic acid are prepared. 6-Aminoquinoline and (II) in $\text{C}_5\text{H}_5\text{N}$ give (after hydrolysis) 6-sulphanilamidoquinoline, m.p. 201° (cf. Bobrański, A., 1939, II, 179). (I) and PhNCS in EtOH afford $p\text{-phenylthiocarbamidobenzenesulphonamide}$, m.p. 189°. 4:4'-Diaminodiphenyl sulphone and $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NCS}$ in EtOH give 4:4'-di(allylthiocarbamido)diphenyl sulphone, m.p. 183°. Sulphanil-*p*-aminoanilide appears to have m.p. 137–138° or 155° (cf. lit.). (II) and $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in $\text{C}_5\text{H}_5\text{N}\cdot\text{COMe}_2$ yield *o*-nitrosulphanilamide, m.p. 167°. 2-Chloroquinoline-3-carboxylic acid and (I) at 165–170° afford $N^4\text{-(3-carboxy-2-quinolyl)sulphanilamide}$, m.p. >280°. 2:8-Diaminoacridine and (II) in $\text{C}_5\text{H}_5\text{N}\cdot\text{COMe}_2\cdot\text{H}_2\text{O}$ give (after hydrolysis with aq. NaOH) 2:8-di(sulphanilamido)acridine (III). Similarly prepared is 2-*p*- $N^1\text{-sulphanilamidobenzenesulphonamidopyridine}$ (IV), m.p. 236–238°. 2-Aminothiazole affords 2-sulphanilamidothiazole, m.p. 197–198° (improved prep.) (cf. Fosbinder *et al.*, A., 1939, II, 525). The protective action of the latter and (III) in streptococcal and pneumococcal infections in mice is noted; (IV) has little effect. 4-Amino-uracil or -thiouracil (V) and diazotised (I) in aq. NaOH afford 4-amino-5-benzeneazo-uracil- or -thiouracil-4'-sulphonamide, respectively. Diazotised 2-sulphanilamidopyridine and (V) or $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ afford analogous dyes. Cholesteryl chloride does not react with (I). The relation between activity and chemical constitution is discussed. A. T. P.

Reduction of dinitroveratrole with sodium sulphide. B. K. NANDI (Current Sci., 1940, 9, 118—119).—1 : 2 : 4 : 5- $C_6H_2(OMe)_2(NO_2)_2$ with aq. $EtOH-Na_2S$ yields 1 : 2 : 4 : 5- $C_6H_2(OMe)_2(NH_2)_2$ and the Na salt, m.p. 194° , of 5-nitro-4-hydroxylamino-veratrole, m.p. 110° . F. R. G.

Manufacture of benzidine.—See B., 1940, 430.

Copper lakes of azo-dyes. Further types. W. F. BEECH and H. D. K. DREW (J.C.S., 1940, 608—612; cf. A., 1938, II, 180).—1-2'-Hydroxy-5'-sulphobenzeneazo- β -naphthol (2 mols.) and aq. $CuCl_2 \cdot 2H_2O$ (3 mols.) give a *Cu complex dodecahydrate* [probably (I)] (the NH_4 salt, $+8H_2O$, has 2 NH_3



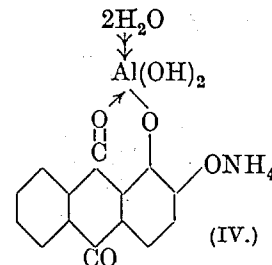
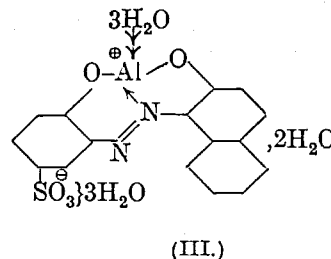
co-ordinated to outer Cu atoms). Both azo-N are in the *anti*-form in both dye residues. This is the first case where both N of an azo-group are co-ordinated to metallic atoms at the same time, i.e., are co-ordinatively saturated. 2 Cu of (I) are each singly ionised and co-

ordinated with 3 other atoms. 1-2'-Hydroxy-5'-sulphobenzeneazo- β -naphthol-6-sulphonic acid and $CuCl_2 \cdot 2H_2O$ in aq. $EtOH$ afford the Cu complex (II), $+5.5$ or $6H_2O$, sol. in H_2O . This is the first case of a lake where 2 atoms of a bivalent metal are combined with 1 azo-residue. In (I) and (II), the aromatic nuclei bearing

o-OH have rotated to bring the OH on opposite sides of the azo-chain; the simple Cu lakes from dyes free from SO_3H have 2 OH on the same side of the azo-chain (*loc. cit.*). The Cu derivative, $C_{17}H_{10}O_3N_2Cu \cdot Cu(OH)_2$, of benzeneazo- β -naphthol-2'-carboxylic acid (*loc. cit.*) is probably the *cupri-hydroxide complex* (formula given). Both types of lake can thus be prepared from the same azo-dye under different conditions of acidity. 2-2'-Carboxybenzeneazo- α -naphthol-4-sulphonic acid and aq. $CuCl_2 \cdot 2H_2O$ yield a *Cu complex dihydrate*, $C_{17}H_{10}O_6N_2SCu \cdot 2H_2O$ (1 Cu : 1 azo-dye residue). Formation of the NH_4 salt, $+4H_2O$, involves change of structure involving removal of one third of its azo-dye residues and co-ordination with NH_3 (formula suggested); left in air for 2 weeks, it loses $\sim 4H_2O + 2NH_3$. 2-Benzeneazo- α -naphthol-4-sulphonic acid and aq. $CuCl_2$ afford the simple Cu salt, $+8H_2O$. Action of aq. NH_3 on the Cu salt, $+8H_2O$, from 1-3'-sulphobenzeneazo- β -naphthol causes the Cu to wander to the inner complex to give an NH_4 salt of a *cupri-hydroxide complex* with loss of 1 dye residue.

1-2'-Hydroxy- or -carboxy-benzeneazo- β -naphthylamine yields anhyd. *Cu complexes*, $C_{16}H_{11}ON_3Cu$ (C_5H_5N derivative; base co-ordinated to Cu) or $C_{17}H_{11}O_2N_3Cu$ (III) [C_5H_5N derivative in moist air gives the *monohydrate* of (III)], respectively. The azo-dyes are able to adjust their configurations to conform with the structural requirements of substituents in the nuclei and with the valency of the lake-forming metal. A. T. P.

Structure of aluminium lakes of azo-dyes and of alizarin. W. F. BEECH and H. D. K. DREW (J.C.S., 1940, 603—607; cf. A., 1939, II, 309).—As in case of Cr, no definite lakes of Al with *o*-monohydroxyazo-dyes are isolable; if formed they are unstable. *oo'*-Dihydroxyazo-compounds give lakes similar in structure to those of Cr^{III} , but much less stable to mineral and org. acids. 1-*o*-Hydroxybenzeneazo- β -naphthol (I) and $AlCl_3 \cdot 6H_2O$ in 96% $EtOH$ give the *aluminichloride pentahydrate* (II), $C_{16}H_{20}O_7N_2AlCl$, and a little of a *complex*, probably $[Al(C_{16}H_{10}O_2N_2)_2]H_2 \cdot 2H_2O$. The aq. solution of (II) contains Cl. At 150° , 5 H_2O and part of the Cl (as HCl) are lost. (II) and aq. NH_3 or K_2CrO_4 , or (I)- $AlCl_3 \cdot 6H_2O$ -NaOH-96% $EtOH$ afford the *oxide tetrahydrate*, $C_{32}H_{28}O_9N_4Al_2$, insol. in H_2O ; 3 H_2O are lost at 120° to give probably the anhyd. hydroxide. 1-2'-Hydroxy-5'-sulphobenzeneazo- β -naphthol and $Al_2(SO_4)_3 \cdot 18H_2O$ in aq. NaOH (+ a little $EtOH$) give the *alumi-sulphonate octahydrate* (III) (NH_4 salt *hexahydrate*), sol. in H_2O ; at 180° it loses $\sim 7.5H_2O$



and becomes almost insol. in H_2O ; aq. HCl yields the azo-dye. 2'-Hydroxy-4'-sulphonaphthalene-1' : 4-azo-1-phenyl-3-methylpyrazol-5-one and aq. $AlCl_3 \cdot 6H_2O$ give the *alumi-sulphonate hexahydrate*, $C_{20}H_{25}O_{11}N_4SAl$ (NH_4 salt *pentahydrate*); it loses 5 H_2O at 180° but regains 2 H_2O in moist air. No pure Al lake is obtained from *o*-carboxybenzeneazo- β -naphthol or benzeneazosalicylic acid, although there is evidence of formation of lakes containing 1 Al : 1 dye residue. Alizarin and $AlCl_3 \cdot 6H_2O$ -NaOH in $EtOH$ afford a *substance*, $C_{28}H_{19}O_{17}Al_5 \cdot 13H_2O$ (formula suggested), converted by dil. aq. NH_3 into an insol. substance and a red lake, $C_{14}H_{21}O_{12}NAl_2$, or by aq. NH_3 (d 0.88) into NH_4Al *alizarate dihydrate* [probably (IV)]; it loses $\sim 3H_2O + 1NH_3$ at 170° ; aq. HCl regenerates alizarin. Alizarin and $CaCO_3$ in boiling H_2O give Ca alizarate dihydrate. The structure of Turkey-red Al-Ca lake is discussed.

A. T. P.

Method of diazotisation.—See B., 1940, 430.

Manufacture of stable diazo-salts.—See B., 1940, 430.

Azo-group as a chelating group. IV. Constitution of arylazobisoximes. (Miss) M. ELKINS and L. HUNTER (J.C.S., 1940, 653—655; cf. A., 1938, II, 483).—Support for Bamberger's hydroxytriazene structure for the arylazobisoximes is provided by the prep. of co-ordinated Cu^{II} , Ni , Co^{II} , and Fe^{III} complexes of type A ($\text{X} = \text{CR}_2\text{N}\cdot\text{O}\cdot\text{CR}_2$). Thus, benzeneazobisacetoxime gives Cu^{II} , m.p. 175—178°, Ni , m.p. 166° (*dipyridino*-compound, m.p. $\sim 108^\circ$, loses 2 $\text{C}_5\text{H}_5\text{N}$ at $\sim 80^\circ$ or in air), Co^{II} , m.p. 148°, and Fe^{III} , m.p. 138°, compounds. *o*-Tolueneazobisacetoxime, m.p. 78—82°, yields Cu^{II} , m.p. 131°, Ni , m.p. 143°, Co^{II} , m.p. 128°, and Fe^{III} , m.p. 125°, compounds. *p*-Tolueneazobisacetoxime, m.p. 143°, affords Cu^{II} (*anhyd.*, m.p. 181°; *monohydrate*, m.p. 180°), Ni , m.p. 174° (*dipyridino*-compound loses 2 $\text{C}_5\text{H}_5\text{N}$ at $\sim 110^\circ$), and Fe^{III} , m.p. 136—137°, compounds. Benzeneazobismethyl-ethylketoxime, m.p. 92—93°, yields Cu^{II} , m.p. 106°, Ni , m.p. 101° (*dipyridino*-compound, m.p. 80°), Co^{II} ($+2\text{H}_2\text{O}$), m.p. 115—118°, and Fe^{III} , m.p. 88—90°, compounds. *m*-Tolueneazobismethyl-ethylketoxime, m.p. 50—51° (from *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$ and COMeEt in alkali), yields Cu^{II} ($+ \text{H}_2\text{O}$), m.p. 86—88° (*anhyd.*, m.p. 103—105°), Ni , m.p. 80—82°, Co^{II} , m.p. 80—85°, and Fe^{III} , m.p. $\sim 50^\circ$, compounds. Benzeneazobisbenzaloxime, new m.p. 132—134°, gives Cu^{II} , m.p. 187°, Ni , m.p. 168° (*dipyridino*-compound, m.p. 150—155°), Co^{II} , m.p. 80—85°, and Fe^{III} (impure), m.p. 110° (softens at 80°), compounds. There is only momentary formation of Co^{III} complexes. The complexes are decomposed by mineral acids but are stable to boiling aq. or alcoholic alkali. A. T. P.

Apparatus for continuous automatic measurement of evolved gas.—See A., 1940, I, 302.

Ethers of phenylmethylcarbinol and its homologues.—See B., 1940, 431.

Resolution of β -naphthylmethylcarbinol. T. A. COLLYER and J. KENYON (J.C.S., 1940, 676—679).—*dl*- β - $\text{C}_{10}\text{H}_7\cdot\text{CHMe}\cdot\text{OH}$ (Lund, A., 1937, II, 364) affords a *H* phthalate (I), m.p. 125°, and thence the *cinchonidine* salt, m.p. 167° (decomp.), $[\alpha]_{5893} -41.0^\circ$ in CHCl_3 , of *d*- β -naphthylmethylcarbinyl *H* phthalate (II), m.p. 101—102°. Decomp. of the mother-liquors and conversion into the *strychnine* salt, m.p. 200—202°, $[\alpha]_{5893} -45.3^\circ$ in CHCl_3 , affords *l*- β -naphthylmethylcarbinyl *H* phthalate (III), m.p. 101—102°. Hydrolysis (aq. $\text{EtOH}\cdot\text{NaOH}$) of (II) and (III) gives *d*-, m.p. 71—72° (formate, m.p. 62—64°, $[\alpha]_{5893} +10.5^\circ$ in EtOH ; *acetate*, m.p. 36—37°, $[\alpha]_{5893} +124.2^\circ$ in EtOH), and *l*- β - $\text{C}_{10}\text{H}_7\cdot\text{CHMe}\cdot\text{OH}$ (IV), m.p. 71—72° (*benzoate*, m.p. 62—64°, $[\alpha]_{5893} -53.4^\circ$ in EtOH), respectively. Both are optically pure. Vals. of $[\alpha]$ are compared with those of the corresponding derivatives of α - $\text{C}_{10}\text{H}_7\cdot\text{CHMe}\cdot\text{OH}$ (cf. Pickard *et al.*, J.C.S., 1914, 105, 2644). Both *l*- α - and *l*- β -derivatives of C_{10}H_8 are configuratively similar and optical behaviour of both series of compounds is dominated by C_{10}H_7 . (III) and $\text{AcOH}\cdot\text{NaOAc}$ at 100° (bath) for ~ 40 hr. afford (I) + (III) and the acetate (activity 6.5% without inversion of configuration) of (IV); after ~ 20 hr. the *l* + *dl*-acetate, $[\alpha]_{5461} -8.8^\circ$ in EtOH , and *H* phthalate, $[\alpha]_{5461} +27^\circ$ in EtOH , are recovered.

(III) and anhyd. HCO_2H rapidly afford *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and *dl*- β -naphthylmethylcarbinyl formate, m.p. 55—56°. A. T. P.

Hydrogenation of wood. H. P. GODARD, J. L. MCCARTHY, and H. HIBBERT (J. Amer. Chem. Soc., 1940, 62, 988).—Hydrogenation (3.2 H_2 per 100 g.; Cu chromite; dioxan; 250—280°/333—400 atm.) of resin- and fat-free maple and spruce wood meal gives 60—70% and 35—40% (calc. on total lignin), respectively, of 4-*n*-propylcyclohexanol + 1:2-diol with oils of higher b.p. R. S. C.

Biochemistry of micro-organisms. LXV. (A) Chlorine metabolism by moulds. (B) Caldariomycin, $\text{C}_5\text{H}_8\text{O}_2\text{Cl}_2$, a metabolic product of *Caldariomyces fumago*, Woronichin. P. W. CLUTTERBUCK, S. L. MUKHOPADHYAY, A. E. OXFORD, and H. RAISTRICK (Biochem. J., 1940, 34, 664—677).—A quant. survey of the Cl metabolism of 139 species or strains of moulds grown on Czapek-Dox 5% glucose solution containing 0.5 g. of KCl per l. as sole source of Cl shows that extensive conversion of inorg. chloride into org. metabolic products containing Cl is of rather rare occurrence although with a no. of species this conversion is by no means negligible. Under these conditions *C. fumago* affords fumaric acid and caldariomycin (I), m.p. 121°, $[\alpha]_{\text{D}}^{20} +59.2^\circ$ in H_2O , which is probably 2:2-dichlorocyclopentane-1:3-diol. It does not contain OMe or Me as side-chain. The Cl atoms are very labile since they are completely removed when it is kept overnight in cold 0.1N-NaOH. It does not contain CO or CHO but since it has two active H (Zerevitinov) the probable presence of two actual or potential OH is indicated although no satisfactory derivatives proving the presence of these groups could be obtained. It is oxidised by CrO_3 to succinic acid, thus establishing the presence of $:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:$. It is reduced (H_2 , Pd-C, H_2O) to cyclopentanone. $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{OH}$ cannot be present since it is not attacked by HIO_4 . It is very stable to heat and does not lose H_2O or HCl at a moderate temp. Above 180° it gives H_2O , HCl, black resinous products, and two isomeric ketones, $\text{C}_5\text{H}_8\text{OCl}$, which yield dinitrophenylhydrazones, m.p. 226° (decomp.) and 238° (decomp.); the former is also obtained from the products of hydrolysis of caldariomycin by boiling 2N- H_2SO_4 . It does not contain $\cdot\text{CH}_2\cdot\text{CO}\cdot$ since it gives no ketonic reactions. This group is formed by treatment with dil. alkali hydroxide since the solution then gives a ppt. with Brady's reagent. Further, (I) does not immediately give Callow's modification of the Zimmermann reaction for active CH_2 although an alkaline solution after some time quickly gives an intense reaction. Finally, the reduction of cold Fehling's solution by (I) is apparent only after a considerable lag period during which a reducing substance is presumably formed. H. W.

Action of ephedrine on halogenated organic compounds.—See B., 1940, 493.

Reaction between dibenzyl disulphide and sulphuryl chloride. G. H. ELLIOTT and J. B. SPEAKMAN (J.C.S., 1940, 641—649).— $(\text{CH}_2\text{Ph}\cdot\text{S})_2$ (I) and SO_2Cl_2 in H_2O -free Et_2O or C_6H_6 at 37—39° afford CH_2PhCl and SO_2 , with some S (not formed with excess of SO_2Cl_2). In undried Et_2O , reaction is slow

at room temp. but at the b.p. similar fission may occur; (I) is partly oxidised to $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ (II), the yield of which decreases with excess of SO_2Cl_2 since at 37—39° (II) and SO_2Cl_2 (excess) give CH_2PhCl (mainly), $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Cl}$, and SO_2 . Fission of (I) without conversion into (II) may occur. Dibenzyl disulphide could not be prepared, but di-*p*-tolyl disulphide is unchanged with SO_2Cl_2 in C_6H_6 at 58—60°, although the corresponding disulphide with SO_2Cl_2 in Et_2O affords *p*- $\text{C}_6\text{H}_4\text{ClMe}$. Mechanisms of reactions are discussed. H_2O may facilitate the action of SO_2Cl_2 on wool by swelling the fibres. Disulphide bond breakdown occurs; SO_2Cl_2 , like Cl_2 , renders wool unshrinkable probably by rupture of the cystine linkages between the peptide chains of the fibres. SOCl_2 , unsuitable for making wool unshrinkable, has no significant action on (I) or (II) at 37—39°.

A. T. P.

Separated auxo-enoid systems. X. Colour phenomena of nitrocinnamoyl derivatives of arylamines. E. A. SMIRNOV (J. Gen. Chem. Russ., 1940, 10, 43—54).— $\text{C}_6\text{H}_4\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$ and $\text{NH}_2\cdot\text{C}_6\text{H}_4\text{R}'$ give the following $\text{C}_6\text{H}_4\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{R}'$: R = H : R' = m-, m.p. 115°, and *p*-OMe, m.p. 149°; R' = m-, m.p. 218°, and *p*-OH, m.p. 213°; R' = m-, m.p. 183·5°, and *p*-NMe₂, m.p. 173·5°; R = *m*-NO₂ : R' = H, m.p. 199·5°; R' = m-, m.p. 174°, and *p*-OMe, m.p. 192·5°; R' = m-, m.p. 275·5°, and *p*-OH, m.p. 258·5° (N-Me derivative, m.p. 213°); R' = m-, m.p. 194·5°, and *p*-NMe₂, m.p. 222°; R = *p*-NO₂ : R' = H, m.p. 208·5°; R' = m-, m.p. 178°, and *p*-OMe, m.p. 215·5°; R' = m-, m.p. 254·5°, and *p*-OH, m.p. 279° (N-Me derivative, m.p. 226°); R' = m-, m.p. 224·5°, and *p*-NMe₂, m.p. 238·5°. The intensity of coloration (yellow to dark red) of the compounds rises in the order R = H < *m*-NO₂ < *p*-NO₂, and R' = H < *m*-OMe < *p*-OMe < *m*-OH < *p*-OH < *m*-NMe₂ < *p*-NMe₂.

R. T.

Constitution of dihydroxy-homophthalic acid and -terephthalic acid derived from triethyl orcinoltricarboxylate. Y. ASAHINA and H. NOGAMI (Proc. Imp. Acad. Tokyo, 1940, 16, 119—121).—3 : 5-Dihydroxy-2-carboxyphenylacetic acid is converted by CH_2N_2 into the Me₂ ester, m.p. 77°, which with MeI and K_2CO_3 in COMe₂ affords Me 3 : 5-dimethoxy-2-carbomethoxyphenylacetate, m.p. 72—73°, hydrolysed (KOH-EtOH) to 3 : 5-dimethoxy-2-carbomethoxyphenylacetic acid, m.p. 147·5°. The corresponding chloride is condensed with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ and the product is transformed by NH_3 into Et γ -3 : 5-dimethoxy-2-carbomethoxyphenylacetate (I), m.p. 115°, which is converted by restrained action of KOH into 3 : 5-dimethoxy-2-carbomethoxybenzyl Me ketone, m.p. 100·5°, and thence by conc. H_2SO_4 into the corresponding acid, m.p. 139—140°, which is not readily lactonised. Successive treatments of (I) with BuI and EtOH-NaOEt, KOH-EtOH, and conc. H_2SO_4 or KOH-EtOH give a product, m.p. 137°, quite distinct from olivetonic acid Me₂ ether, m.p. 93°. Jerdan's orientation (J.C.S., 1899, 75, 808) of the orcinoldicarboxylic acids must therefore be reversed. Et 3 : 5-dihydroxy-4-carboxy-2-carbomethoxyphenylacetate has been con-

verted into 6 : 8-dimethoxy-3-methylisocoumarin and 3 : 5-dihydroxy-2-carbomethoxyphenylacetic acid into olivetonic acid or olivetonide Me₂ ether. H. W.

Naphthalene series. II. Synthesis of *trans*-decahydronaphthalene-*trans*-2-carboxylic-3-acetic acid. N. A. CHAUDHRY, R. D. DESAI, and G. S. SAHARIYA (Proc. Indian Acad. Sci., 1940, 11, A, 145—148).—*trans*-2-Ketodecahydronaphthalene gives the *cyanohydrin*, b.p. 113°/6 mm., dehydrated by $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$ at 0°—room temp. to *trans*-2-cyano- Δ^2 -octahydronaphthalene, b.p. 145°/6 mm. [oxidised by KMnO_4 to cyclohexane-1 : 2-diacetic acid (I)]. Boiling conc. HCl then gives *trans*- Δ^2 -octahydronaphthalene-2-carboxylic acid, m.p. 146° [oxidised to (I)], which with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et-EtOH}$ at, successively, 0°, room temp., and the b.p. gives an ester, hydrolysed to *trans*-decahydronaphthalene-*trans*-2-carboxylic-3-acetic acid, m.p. 214—215°, and an impure acid, m.p. 160—180°.

R. S. C.

Mechanism of aromatic side-chain reactions with special reference to polar effects of substituents.—See A., 1940, I, 295.

Naphthalene series. I. Properties of 2-acetyl-1-naphthol. Synthesis of 2-ethyl-1-naphthol. M. AKRAM, R. D. DESAI, and A. KAMAL. III. Properties of 4-acetyl-1-naphthol. Preparation of 4-ethyl-1-naphthol. IV. Preparation and properties of 2 : 4-diacetyl- and 2-acetyl-4-propionyl-1-naphthol. M. AKRAM and R. D. DESAI (Proc. Indian Acad. Sci., 1940, 11, A, 139—144, 149—155, 156—161).—I. Some (4 : 1-OH·C₁₀H₆)₂, m.p. 300°, and 1 : 1'-dihydroxy-2 : 2'-dinaphthyl oxide, m.p. 183—184°, accompany (method : Clemo *et al.*, J.C.S., 1931, 1265) 2 : 1-C₁₀H₆Ac·OH (I) (blue-green FeCl₃ colour; *picrate*, m.p. 112°; *semicarbazone*, m.p. 306°; *phenylhydrazine*, m.p. 141°). Anhyd. AlCl₃ converts (I) in PhNO₂ into a compound, C₂₄H₁₈O₄, m.p. >300° : 2 : 4 : 1-C₁₀H₅AcBr·OH, Ac₂O, and NaOAc at 180—185° give 6-bromo-3-acetyl-2-methyl-1 : 4- α -naphthopyrone, m.p. 206—207°, hydrolysed by 10% NaOH to 1 : 4 : 2-OH·C₁₀H₅Br·CO₂H (II). Br and (I) in CHCl₃ give 4-bromo-2-bromoacetyl-1-naphthol, m.p. 150°, hydrolysed by NaOEt in boiling EtOH to 4-bromo-2-hydroxyacetyl-1-naphthol, m.p. 136—137°, and 4-bromo- α -naphthacoumaranone, m.p. 274°. 4-Bromo-2-dibromoacetyl-1-naphthol (similarly prepared), m.p. 199°, and NaOEt-EtOH give (II) and a neutral substance, m.p. 250°. 4 : 2 : 1-NO₂·C₁₀H₅Ac·OH and NaOAc-Ac₂O at 100—140° give 6-nitro-3-acetyl-2-methyl-1 : 4- α -naphthopyrone, m.p. 242—243°, hydrolysed by hot 10% NaOH to 4 : 1 : 2-NO₂·C₁₀H₅(OH)·CO₂H. Zn-Hg-HCl reduces (I) to 2 : 1-C₁₀H₆Et·OH, m.p. 70° (lit. 68°) [*picrate*, m.p. 123° (lit. 118°); *Me ether*, b.p. 136°/6 mm. (*picrate*, m.p. 80°); 4-NO₂-, m.p. 88°, and PhN₂-derivative, m.p. 189°; with Br gives 2- β -bromoethyl-1-naphthol, m.p. 90° (with alkali gives a substance, m.p. 280° after sintering)], and 2-ethyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol, b.p. 108°/8 mm.

III. 4 : 1-C₁₀H₆Ac·OH (III), m.p. 199—200° (*acetate*, m.p. 83—84°; *Me ether*, m.p. 71—72°; *picrate*, m.p. 160—161°; *semicarbazone*, m.p. 200°; *oxime*, m.p. 250°), with a little (I) is best obtained from α -C₁₀H₇·OH by AcCl and ZnCl₂ in PhNO₂ at

room temp. With ZnCl_2 and boiling EtCO_2H it gives 1:2-OH· C_{10}H_6 ·COEt. With Br-CHCl_3 it gives 2-bromo-4-acetyl-, m.p. 134—135°, 4-bromoacetyl-, m.p. 140° [with warm EtOH gives (colour changes) a substance, m.p. 178—180°; with boiling 10% NaOH gives the 4-hydroxyacetyl derivative, m.p. 93—94°], and 4-dibromoacetyl-1-naphthol, m.p. 116° (with 10% NaOH gives 3-bromo-4-hydroxy-1-naphthoic acid, m.p. 208°). With NaOBr it gives 4:1-OH· C_{10}H_6 · CO_2H , which in boiling H_2O or above the m.p. gives α - C_{10}H_7 ·OH and with Br-CHCl_3 gives 4:1- C_{10}H_6 ·Br·OH. With HNO_3 (d 1.5) in AcOH it gives 2-nitro-4-acetyl-1-naphthol (IV), m.p. 145°, 2:1- NO_2 · C_{10}H_6 ·OH, and 2:4:1-(NO_2) $_2$ · C_{10}H_5 ·OH [also obtained from (IV)]. With Zn-Hg-HCl it gives 4:1- C_{10}H_6 ·Et·OH, m.p. 42°, b.p. 160—161°/7 mm. [with PhN_2Cl gives 2-benzeneazo-4-ethyl-1-naphthol, m.p. >300°, and (? cis- and trans-)forms, m.p. 111—112° and 180—181°, of 4-ethyl-1:2-naphthoquinone-2-phenylhydrazones], and 4-ethyl-1:2:3:4-tetrahydro-1-naphthol, b.p. 110—111°/10 mm.

IV. AcCl-AlCl_3 in PhNO_2 converts (I) or (III) into 2:4-diacetyl-1-naphthol (V), m.p. 141°, which yields (methods as above) 2-acetyl-4-bromoacetyl-, m.p. 164—165°, 2-acetyl-4-hydroxyacetyl-, m.p. 130°, and 2-bromoacetyl-4-dibromoacetyl- (VI), m.p. 136°, -1-naphthol. Boiling 10% NaOH converts (VI) into α -naphthacoumaranone-4-carboxylic acid, m.p. 207—209°. With HNO_3 (d 1.5) (1 mol.) in AcOH, (V) gives 4:2:1- and 2:4:1- NO_2 · C_{10}H_5 ·Ac·OH and 2:4:1-(NO_2) $_2$ · C_{10}H_5 ·OH, obtained also with a polynitro-compound, m.p. 215°, by use of 2 mols. of HNO_3 . With ZnCl_2 in boiling AcOH or EtCO_2H , (V) gives 2:1- C_{10}H_6 ·R·OH (R = Ac or EtCO, respectively), and with NaOAc-Ac $_2$ O at 180—190° gives 3:6-diacetyl-2-methyl-1:4- α -naphthopyrone, m.p. 170—171°, hydrolysed by boiling 10% NaOH to 1-hydroxy-4-acetyl-2-naphthoic acid, m.p. 216° [decomp. to (III)]. With EtCOCl and ZnCl_2 in PhNO_2 , (I) gives 2-acetyl-4-propionyl-1-naphthol, m.p. 131°, the Br-derivative, m.p. 141°, of which loses its Br to hot 5% NaOH, with ZnCl_2 -AcOH gives (I), with ZnCl_2 - EtCO_2H gives 1:2-OH· C_{10}H_6 ·COEt, and with HNO_3 (1 mol.) gives 4:2:1- NO_2 · C_{10}H_5 ·Ac·OH with a little 2:1- NO_2 · C_{10}H_6 ·OH and 2:4:1-(NO_2) $_2$ · C_{10}H_5 ·OH.

R. S. C.

Preparation and properties of α - and β -naphthylglyoxal. L. N. GOLDIREV and I. J. POSTOVSKI (J. Gen. Chem. Russ., 1940, 10, 39—42).—1- or 2- C_{10}H_7 ·COMe with SeO_2 in 80% AcOH (1 hr. at the b.p.) yields α - (I), an oil (+ H_2O , m.p. 82°; osazone, m.p. 105°), or β -naphthylglyoxal (II) [+ H_2O , m.p. 110° (lit. 98°); osazone, m.p. 134°], respectively. (I) and (II) with o - $\text{C}_6\text{H}_4(\text{NH}_2)_2$ yield the corresponding quinoxalines, m.p. 114° and 137°, respectively. (II) and CH_2O in aq. NH_3 [$\text{Cu}(\text{OAc})_2$ catalyst] afford 4- β -naphthylglyoxaline, m.p. 168°. (I) and (II) give an intense green coloration when heated with 2-aminopyridine.

R. T.

Derivatives of 2-phenylcyclohexanone. J. C. BARDHAN (Chem. and Ind., 1940, 369).— $\text{CPhNa}(\text{CO}_2\text{Et})_2$ and $\text{CH}_2\text{Ac-CH}_2\text{-NMcEt}_2\text{I}$ give Et δ -keto- α -carbethoxy- α -phenylhexoate, b.p. 182°/6

mm., hydrolysed and decarboxylated to δ -keto- α -phenylhexoic acid, b.p. 180°/4 mm., 185°/6 mm. [semicarbazone, m.p. 161—162°; Me ester, b.p. 149°/5 mm. (semicarbazone, m.p. 151—152°)]. The Et ester, b.p. 160°/9 mm. (semicarbazone, m.p. 119—120°), condenses with $\text{CN-CH}_2\text{-CO}_2\text{Et}$ (piperidine) to Et_2 α -cyano- ϵ -phenyl- β -methyl- Δ^4 -pentene- α -dicarboxylate, b.p. 212°/7 mm., which when treated with KCN and then hydrolysed and esterified yields Et_3 α -phenyl- δ -methylpentane- $\alpha\delta\epsilon$ -tricarboxylate, b.p. 208°/7 mm. This is subjected to the Dieckmann reaction and the resulting β -CO-ester is condensed with $\text{CH}_2\text{Cl-CH}_2\text{-CO}_2\text{Et}$; the crude product is hydrolysed (conc. HCl) and purified through Et β -2-keto-4-carbethoxy-1-phenyl-4-methylcyclohexylpropionate. Similarly p -OMe- $\text{C}_6\text{H}_4\text{-CH}(\text{CO}_2\text{Et})_2$ affords successively Et δ -keto- α -carbethoxy- α -anisylhexoate, b.p. 202°/6 mm., δ -keto- α -anisylhexoic acid, b.p. 200°/5 mm. (Et ester, b.p. 180°/8 mm.), Et_2 α -cyano- ϵ -anisyl- β -methyl- Δ^4 -pentene- α -dicarboxylate, b.p. 230°/6 mm., Et_3 α -anisyl- δ -methylpentane- $\alpha\delta\epsilon$ -tricarboxylate, b.p. 228°/6 mm., and Et β -2-keto-4-carbethoxy-1-anisyl-4-methylcyclohexylpropionate, b.p. 221°/5 mm.

H. W.

Synthesis of β -phenylnaphthalene derivatives.

M. WEIZMANN, E. BERGMANN, and E. BOGRACHOV (Chem. and Ind., 1940, 402—403; cf. Hey *et al.*, A., 1940, II, 168, 188).— Ph_2 , $(\text{CH}_2\text{-CO})_2\text{O}$, and AlCl_3 in PhNO_2 yield γ -keto- γ - p -diphenylbutyric acid, m.p. 183°, reduced (Clemmensen-Martin; A., 1936, 1249) to γ - p -diphenylbutyric acid (I), m.p. 118° (no 2-substituted product isolated), and a product, m.p. 328°. SOCl_2 followed by AlCl_3 in PhNO_2 converts (I) into 1-keto-7-phenyl-1:2:3:4-tetrahydronaphthalene, m.p. 70°, reduced as above and then dehydrogenated (Se) to 2- C_{10}H_7 ·Ph.

A. Lr.

Production of polycyclic aromatic types through the cyclodehydration of unsaturated ketones. W. S. RAPSON and R. G. SHUTTLEWORTH (J.C.S., 1940, 636—641).—1-Keto-1:2:3:4-tetrahydronaphthalene (I) (cf. Hartmann *et al.*, A., 1933, 61) and PhCHO in 4% KOH-EtOH yield the 2- CHPh derivative, m.p. 105°, b.p. 210—212°/2 mm., converted by P_2O_5 in xylene into 3:4-benzfluorene. 1-Keto-2- o -tolylidene-1:2:3:4-tetrahydronaphthalene, m.p. 68°, b.p. 213°/2 mm., affords (similarly or by NaNH_2) 8-methyl-3:4-benzfluorene, m.p. 104—105°, b.p. 203°/2 mm., purified through the picrate, m.p. 127—128°, and oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ -AcOH to the benzfluorenone, m.p. 139.5—140.5°. cycloHexanone and o - $\text{C}_6\text{H}_4\text{Me-CHO}$ in 4% aq. KOH give 2- o -tolylidene-, m.p. 66—67°, b.p. 151—154°/4 mm., and 2:6-di- o -tolylidene-cyclohexanone, m.p. 138—139° (main product in KOH-EtOH); neither the former nor o -tolylideneacetophenone is dehydrated by P_2O_5 or NaNH_2 . (I), 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\text{-CHO}$, and 4% KOH-EtOH afford 1-keto-2-(2':4':6':trimethylbenzylidene)-1:2:3:4-tetrahydronaphthalene, m.p. 92—92.5°, dehydrated by P_2O_5 in xylene to three dihydro-5:7-dimethyl-1:2-benzanthracene, m.p. 146—147° (II) (picrate, m.p. 190—191°), m.p. 114°, and m.p. 115.5—116.5° (picrate, m.p. 165°); one may be the 3:4- H_2 -derivative. (II) and Se afford 5:7-dimethyl-1:2-

benzanthracene, m.p. 120—121°. 2-(2':4':6'-*Trimethylbenzylidene*)- α -hydriindone, m.p. 93.5—94.5°, could not be dehydrated. Tetrahydro-*o*-toluonitrile (III) and 95% H_3PO_4 (better than H_2SO_4) at 120—130° afford 6-methyl- Δ^1 -cyclohexenecarboxylic acid (IV), m.p. 105.5° (not identical with that of Mazza *et al.*, A., 1927, 665), oxidised (O_3 followed by 0.1N aq. KMnO_4 in CO_2) to α -methyladipic acid. Boiling aq. KOH - EtOH (9 days) and (III) give an *acid amide*, m.p. 128°, and (IV), but after 1 day yield an *amide*, m.p. 146°, and a (?) polymerised *amide*, m.p. >300°. The *anilide*, m.p. 106.5—107.5°, of (IV) is converted by PCl_5 - PhMe at 100° (bath), then SnCl_2 - HCl - Et_2O , into 6-methyl- Δ^1 -cyclohexenealdehyde, b.p. 66—68°/10 mm. (*semicarbazone*, m.p. 207—209°; 2:4-dinitrophenylhydrazone, m.p. 179°), converted by aq. AgNO_3 - NH_3 into (IV). *cycloHexanone*, $\text{CHMe} \cdot \text{CH} \cdot \text{CHO}$ (V), and 1% aq. KOH in EtOH at <30° give a resin and probably crotonylidenecyclohexanone [*semicarbazone*, m.p. 191° (sinters at 187°)]; the total product and H_2 (Pd- SrCO_3) in MeOH at 1.5—2 atm. afford *cyclohexanol*, 2-*n*-butylcyclohexanol, and a mixture, $\text{C}_{10}\text{H}_{18}\text{O}_2$. *cyclopentanone* and (V) yield a product, $(\text{C}_4\text{H}_6\text{O})_n$, probably a polymeride from (V). Less alkali affords less resin and gives a product, b.p. 115—135°/10 mm.; the latter yields a *semicarbazone*, m.p. 215—216° (decomp.), probably from crotonylidenecyclopentanone. Hydrogenation of the products affords 2-*n*-butylcyclopentanone (VI) (*semicarbazone*, m.p. 185—186°) and a mixture, $\text{C}_9\text{H}_{16}\text{O}_2$. α -*n*-Butyladipic acid, m.p. 59.5° (prepared from Et 5-*n*-butylcyclopentanone-2-carboxylate), on distillation with a little BaO , affords (VI). (V), COMe_2 , and 1% aq. KOH (cold) yield crotonylidenecetone (*semicarbazone*, m.p. 164—166°); the total product was hydrogenated to *Me n*-amyl ketone and a product, C_7H_{14} or C_{16}O_2 (2 reactive H). Probably the ketones react with (V) at the double linking and also at the CO group. A. T. P.

Dehydrogenation. V. S. C. SEN-GUPTA (J. Indian Chem. Soc., 1940, 17, 101—106; cf. A., 1939, II, 538).—*cyclopentane-1-carboxylic-1-acetic anhydride* (I), $\text{C}_{10}\text{H}_{18}$, and AlCl_3 in PhNO_2 give γ -*keto- γ - α* (II), m.p. 140—141° (*Me* ester, m.p. 69—70°; oxidised by NaOBr to α - $\text{C}_{10}\text{H}_7\text{CO}_2\text{H}$), and β -*naphthyl- α -tetramethylenebutyric acid*, m.p. 190—191° (*Me* ester, m.p. 109—110°; with NaOBr gives β - $\text{C}_{10}\text{H}_7\text{CO}_2\text{H}$). Zn - Hg - HCl reduces (II) to 1- β -1'-*naphthylethylcyclopentane-1-carboxylic acid*, m.p. 108—109°, cyclised by H_2SO_4 - H_2O (3:1 vol.) at 100° to 1-*keto-1:2:3:4-tetrahydrophenanthrene-2:2*-spirocyclopentane, b.p. 215°/6 mm. Clemmensen reduction then gives 1:2:3:4-tetrahydrophenanthrene-2:2-spirocyclopentane, b.p. 190—195°/8 mm., which with Se at 300—320° and later 340—350° gives chrysene. 1- $\text{C}_{10}\text{H}_7\text{Me}$ and (I) give only γ -*keto- γ -4-methyl-1-naphthyl- α -tetramethylenebutyric acid*, m.p. 176—177° (with NaOCl gives 4:1- $\text{C}_{10}\text{H}_6\text{MeCO}_2\text{H}$), the *Me* ester, m.p. 56—57°, of which (but not the free acid) is reduced to *Me* 1- β -4'-methyl-1'-*naphthylethylcyclopentane-1-carboxylate*, b.p. 230—235°/5 mm. The derived *acid*, m.p. 112°, gives (as above) 1-*keto-9-methyl*-, m.p. 97°, and thence 9-methyl-1:2:3:4-tetrahydrophenanthrene-2:2-

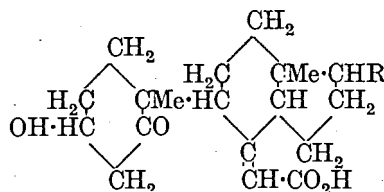
spirocyclopentane, m.p. 69—70°, which with Se gives 3-methyl-1:2-benzanthracene. R. S. C.

Structure of ethanolysis products of spruce and maple wood. L. BRICKMAN, J. J. PYLE, W. L. HAWKINS, and H. HIBBERT (J. Amer. Chem. Soc., 1940, 62, 986).—The "aldehyde fraction" obtained by ethanolysis of maple and spruce wood contains 4-hydroxy-3:5-dimethoxyphenyl and *guaiacyl Me diketone* and not the isomeric *aroyl*acetaldehydes (cf. A., 1939, II, 516). R. S. C.

Sterol group. XL. Bromination of 7-ketocholesteryl acetate. H. JACKSON and E. R. H. JONES (J.C.S., 1940, 659—663; cf. A., 1938, II, 497).—7-Ketocholesteryl acetate (I) and Br (excess) in AcOH afford 5:6-dibromo-7-ketocholestanyl acetate (II), m.p. 146—147° (decomp.), converted by KI-COMe_2 into (I), or by KOAc-AcOH into an impure unsaturated bromo-ketone. Boiling NPhMe_2 and (II) afford 7-keto- $\Delta^{3:5}$ -cholestadiene, also obtained from (I) and HBr-AcOH . (I) and Br-HBr-AcOH yield 3:4:6-tribromo-7-keto- Δ^5 -cholestene (III), decomp. $\sim 143^\circ$, which loses HBr by AgNO_3 - $\text{C}_5\text{H}_5\text{N}$ or KOAc-AcOH at 100°, or NPhMe_2 (less readily), to give 4:6-dibromo-7-keto- $\Delta^{3:5}$ -cholestadiene, m.p. 189—190°. (II) and KI-COMe_2 afford 6-bromo-7-keto- $\Delta^{3:5}$ -cholestadiene, m.p. 117°, unchanged by NPhMe_2 , or $\text{C}_5\text{H}_5\text{N}$, or Zn dust in MeOH or AcOH . 6:6'-Dibromo-7-ketocholestanyl acetate or 7-bromo-6-ketocholestanyl acetate and boiling NPhMe_2 afford 7- or 6-ketocholestanyl acetate, respectively. The effect of substituent Br on light absorption of sterol ketones is discussed. A. T. P.

Hydroxy-ketones of the cyclopentanopolyhydrophenanthrene series.—See B., 1940, 495.

Physiologically active oxidation product of ergosterol. A. F. VON CHRISTIAN (Mikrochem., 1940, 28, 183—185).—Cholesterol and PrCOCl in $\text{C}_5\text{H}_5\text{N}$ give a cholesteryl butyrate (I) which is biologically inactive (cf. A., 1939, III, 598). This is due to oxidation of ergosterol (II), present as impurity, to a product (III) which deactivates the (I). Passage of O_2 into ergosterol in EtOH -hæmatoporphyrin and



light gives, *inter alia*, (III) as an acidic oil, probably having the annexed structure. Girard's reagent *P* separates (III) into an unreactive *cis*- (IV)

(physiologically active at 10^{-9} g. per c.c.) and reactive *trans*-form (V) (physiologically much less active), transformed into one another by irradiation by Ra . Light changes (V) into (IV). At $180^\circ/\text{vac}$. (IV) gives (V). The known corresponding aldehyde (A., 1933, 500; 1939, II, 261) is oxidised to (III) by Ag_2O .

R. S. C.

α - and β -7-Hydroxy-3-ketocholanic acid. S. MIYAZI and H. ISAKA (J. Biochem. Japan, 1939, 30, 297—302).—Chenodeoxycholic acid with $\text{C}_5\text{H}_5\text{N-Ac}_2\text{O}$ at room temp. yields *diacetylchenodeoxycholic acid*, m.p. 230° (*Me* ester, m.p. 128°), and with $\text{abs. HCO}_2\text{H}$ at 100° (bath) gives *diformylchenodeoxycholic*

acid, new m.p. 184° (*Me* ester, m.p. 56—86°), which, with 0.5N-NaOH at room temp. for 4 hr., affords α -3-hydroxy-7-formylcholanolic acid, m.p. 147—149°, oxidised ($\text{AcOH}-\text{CrO}_3$) to the 3-*CO*-acid, m.p. 188—189°, hydrolysed (5% KOH in EtOH) to α -7-hydroxy-3-ketocholanolic acid, m.p. 96°. Diformylursodeoxycholic acid (Iwasaki, A., 1937, II, 20), similarly yields β -3-hydroxy-, m.p. 135°, and β -3-keto-7-formylcholanolic acid, m.p. 126—129°, and β -7-hydroxy-3-ketocholanolic acid, m.p. 115—117°. F. O. H.

Manufacture of progesterone.—See B., 1940, 495.

Preparation of antihæmorrhagic compounds.—See A., 1940, III, 516.

Substituted anthraquinones and aroylbenzoic acids.—See B., 1940, 431.

Detoxication. VII. Biological reduction of *l*-menthone to *d*-neomenthol and of *d*-iso-menthone to *d*-isomenthol in the rabbit. Conjugation of *d*-neomenthol with glucuronic acid. R. T. WILLIAMS (Biochem. J., 1940, 34, 690—697).—About 30—40% of *l*-menthone administered to rabbits is excreted as OH-derivatives conjugated with glucuronic acid (I); a part of the menthone mol. is therefore reduced at the CO group. *d*-isoMenthone is also reduced in the rabbit to *d*-isomenthol (II), isolated as the glucuronide. 67—68% of *d*-neomenthol fed to rabbits is excreted in the urine combined with glucuronic acid; this figure is of the same order as those found for *d*-menthol and (II). A method is described, using a Shaffer-Hartmann reagent, for the determination of conjugated (I) in 1 ml. of urine after feeding menthol derivatives. *d*-Neomenthylglucuronide, m.p. 146°, $[\alpha]_D^{22}$ —14.6° in EtOH, NH_4 *d*-neomenthylglucuronate, $[\alpha]_D$ —6.9° in H_2O or (+1 H_2O) $[\alpha]_D$ —5.9° in H_2O , and *d*-neomenthyl 3:5-dinitrobenzoate, m.p. 155°, $[\alpha]_D^{22}$ +22.6° in CHCl_3 , are new. H. W.

Condensation products from " α -terpinene" and the carenes with maleic anhydride. N. F. GOODWAY and T. F. WEST (J.C.S., 1940, 702—703).—The terpene mixture obtained by dehydration of terpineol with a solution of $\text{H}_2\text{C}_2\text{O}_4$ has been separated into five fractions, the first four of which with maleic anhydride give acids of m.p. 124—131°, and not 158° (cf. Diels *et al.*, A., 1938, II, 330). The hydrocarbon formulated by Diels is Δ^4 - and not Δ^3 -carene.

F. R. S.

Syntheses in the camphane series. V. Synthesis of diethyl [1, 2, 2]dicycloheptanedionedicarboxylate from diethyl cyclopentanone-2:5-dicarboxylate. P. C. GUHA and G. D. HAZRA (J. Indian Chem. Soc., 1940, 17, 107—110; cf. A., 1938, II, 13).—The Na_2 derivative of Et_2 cyclopentan-1-one-2:5-dicarboxylate (improved prep.) and $\text{CH}_2\text{Br}-\text{CO}_2\text{Et}$ in C_6H_6 , first at room temp. and then at the b.p., give *cis*- and *trans*-forms, (I), b.p. 145—160° (145—202°)/3 mm., and (II), b.p. 202—208°/3 mm. or vice versa, of Et_2 cyclopentan-1-one-2:5-dicarboxylate-2-acetate. When distilled, (I) slowly gives (II). Hydrolysis of (I) or (II) by 18% HCl gives Et cyclopentan-1-one-2-acetate. With Na in boiling C_6H_6 , (II) gives Et_2

1-keto-3:6-endoketocyclohexane-2:3-dicarboxylate (decomp. when distilled), which with boiling 18% HCl yields by decarboxylation 1-keto-3:6-endoketocyclohexane-3-carboxylic acid, + H_2O , m.p. 212° [*Me* ester, m.p. 129° (semicarbazone, m.p. 209—210°); reduced (Clemmensen) to an acid, m.p. 118°], and a viscous acid, $\text{C}_7\text{H}_{10}\text{O}_3$ (semicarbazone, m.p. 192°).

R. S. C.

Dependence of optical rotatory power on chemical constitution. XVII. Nitro- and carboxy-aryl derivatives of stereoisomeric methylenecamphors. B. K. SINGH and T. P. BARAT (J. Indian Chem. Soc., 1940, 17, 1—18; cf. A., 1938, II, 149).—Many vals. of $[\alpha]$ in CHCl_3 , C_6H_6 , MeOH, EtOH, COMe_2 , and $\text{C}_5\text{H}_5\text{N}$ of the following compounds are determined: *o*-nitroanilinomethylene-*d*-, m.p. 157—158°, $[\alpha]_D^{25}$ +288.5°, -*l*-, m.p. 158°, $[\alpha]_D^{25}$ —288.0°, and -*dl*-camphor, m.p. 150°; *m*-nitroanilinomethylene-*d*-, new m.p. 181°, $[\alpha]_D^{25}$ +249.6° (cf. Rupe *et al.*, A., 1920, i, 327), -*l*-, m.p. 180—181°, $[\alpha]_D^{25}$ —248.0°, and -*dl*-camphor, m.p. 167—168°; *p*-nitroanilinomethylene-*d*-, m.p. 154—155°, $[\alpha]_D^{25}$ +331.2° (cf. Pope *et al.*, J.C.S., 1909, 95, 171; Rupe *et al.*), -*l*-, m.p. 154—155°, $[\alpha]_D^{25}$ —388.1° in MeOH, and -*dl*-camphor, m.p. 167—168°; *o*-carboxyanilinomethylene-*d*-, m.p. 166—167°, $[\alpha]_D^{25}$ +309.4°, -*l*-, m.p. 167—168°, $[\alpha]_D^{25}$ —309.7°, and -*dl*-camphor, m.p. 113° (cf. Rupe *et al.*); *m*-carboxyanilinomethylene-*d*-, m.p. 219—221°, $[\alpha]_D^{25}$ +310.9° in MeOH, -*l*-, m.p. 219—221°, $[\alpha]_D^{25}$ —311.2° in MeOH, and -*dl*-camphor, m.p. 215—217°; *p*-carboxyanilinomethylene-*d*-, m.p. 280—283°, $[\alpha]_D^{25}$ +335.0° in $\text{C}_5\text{H}_5\text{N}$, -*l*-, m.p. 280—282°, $[\alpha]_D^{25}$ —334.1° in $\text{C}_5\text{H}_5\text{N}$, and -*dl*-camphor, m.p. 283—285° (all above vals. of α are in C_6H_6 unless stated otherwise). Relation between rotatory power (*R*) and chemical constitution or solvent used follows no definite plan. The sequence of *R* of the isomerides of nitroanilino-derivatives is in general *p* > *o* > unsubstituted > *m* in all solvents; with carboxy-derivatives, the order in $\text{C}_5\text{H}_5\text{N}$ is unsubstituted > *p* > *o* > *m*. Vals. of *R* of corresponding *d*- and *l*-forms in all solvents are equal and opposite. The compounds obey the simple dispersion law, $[\alpha] = K(\lambda^2 - \lambda_0^2)$. A. T. P.

Dependence of optical rotatory power on chemical constitution. XVI. Bromo- and iodo-aryl derivatives of stereoisomeric methylenecamphors. B. K. SINGH and B. BHADURI (Proc. Indian Acad. Sci., 1939, 10, A, 359—380).—The optical rotatory powers of *o*- (I), m.p., *l* and *d*, 88—89°, *dl*, 95—96°; *m*- (II), m.p., *l* and *d*, α -form, 162—163°, β -form, 111—113°; *dl*, 175—176°, and *p*-bromo-, m.p., *l* and *d*, 186—187°; *dl*, 186—187°, *m*-, m.p., *l* and *d*, 187—188°; *dl*, 182—183°, and *p*-iodo- (III), m.p., *l* and *d*, 185—186°; *dl*, 193—195°, -anilinomethylenecamphor in CHCl_3 , COMe_2 , C_6H_6 , EtOH, MeOH, and $\text{C}_5\text{H}_5\text{N}$ have been measured. *d*- and *l*-(II) exist in two interconvertible dimorphic forms with identical rotatory dispersion, m.p. 162—163° by slow crystallisation and m.p. 111—113° by rapid crystallisation from MeOH. *m*-Bromoanilinomethylene-*dl*-camphor exists in only one form. *o*-Iodoanilinomethylenecamphor could not be got solid. The effect of chemical constitution on the rotation is discussed. The rotatory power decreases in the order

of dielectric const. of the solvents, $\text{MeOH} > \text{EtOH} > \text{COMe}_2 > \text{C}_5\text{H}_5\text{N} > \text{CHCl}_3 > \text{C}_6\text{H}_6$. For position isomerides the sequence of rotatory power is no halogen $> p > m > o$ in EtOH , COMe_2 , and $\text{C}_5\text{H}_5\text{N}$, and no halogen $> o > m > p$ in CHCl_3 and C_6H_6 . The racemic forms of (I), (II), and (III) are true *dl* compounds.

W. R. A.

Pongamol, new crystalline compound from pongamia oil. S. RANGASWAMI and T. R. SESHADRI (Current Sci., 1940, 9, 179).—The isolation from pongamia oil of *pongamol*, $\text{C}_{17}\text{H}_{11}\text{O}_3 \cdot \text{OMe}$, m.p. 128–129°, a phenol which on reduction ($\text{Mg} + \text{HCl}$) yields a red anthocyanin, on oxidation or hydrolysis yields BzOH , and gives a *p*-nitrobenzoyl derivative, is described.

A. LI.

Chemical constituents of lichens found in Ireland. *Lecanora gangaleoides*. II. T. J. NOLAN and J. KEANE (Sci. Proc. Roy. Dublin Soc., 1940, 22, 199–209; cf. A., 1935, 550).—*L. gangaleoides* contains gangaleoidin (I), atranorin and chloratranorin (ratio 1 : 4), *d*-arabitol, endococcin (II), rhodophyscin (III) (acetate), and a substance, $\text{C}_{26}\text{H}_{21}\text{O}_{10}\text{Cl}_3$ (?) (containing OMe ?), m.p. 231–233° (*Me ether*, m.p. 143–144°), which gives a light purple colour with FeCl_3 and pale yellow with H_2SO_4 ; the presence of H_2O -sol. ester or lactone was not confirmed. (II) yields (III) when boiled with AcOH . (III), which contains no OMe , gives no ppt. with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ in AcOH , and the resulting solution fails to give the colour reactions of (III). (I) is a lactone, $\text{C}_{16}\text{H}_{10}\text{O}_6\text{Cl}_2(\text{OH})(\text{OMe})_2$ (*Me ether*, m.p. 181°). MeOH-KOH opens the ring, giving a *Me ester* [*Me₁ ether*, m.p. 186–187°, obtained by hydrolysing the *Me ether* of (I); *Me₂ ether* (IV) (CH_2N_2), m.p. 141–142°], which when distilled under reduced pressure gives an *isomeride*, m.p. 184–185°. (I) with MeOH-KOH followed by H_2O yields *substances*, $\text{C}_{16}\text{H}_{10}\text{O}_6\text{Cl}_2(\text{OMe})_2 + \text{H}_2\text{O}$, m.p. 197–198°, and $+2\text{H}_2\text{O}$, m.p. 161°, either of which with CH_2N_2 yields (IV). Hydrolysis (MeOH-KOH) of (IV) yields an *acid*, $\text{C}_{14}\text{H}_7\text{OCl}_2(\text{CO}_2\text{H})_2(\text{OMe})_3 \cdot \text{H}_2\text{O}$, m.p. 216–217°, which when heated alone or in HCO_2H gives an *acid*, $\text{C}_{14}\text{H}_8\text{OCl}_2(\text{CO}_2\text{H})(\text{OMe})_3$ (V), m.p. 138–139° (*Me ester*, m.p. 79–80°), when heated in glycerol at 220–225° for 5 hr. gives a *phenol* $\text{C}_{14}\text{H}_9\text{OCl}_2(\text{OH})(\text{OMe})_2$ (VI), m.p. 165–166° (*Me ether*, m.p. 112–113°), and when vac.-distilled gives (V), (VI), and a neutral substance (? a xanthone), $\text{C}_{15}\text{H}_7\text{O}_2\text{Cl}_2(\text{OMe})_3$, m.p. 212–213°. It is concluded that (I) is a derivative of $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO-O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4$, having as substituents 2 Me, 2 Cl, OH, OMe, and CO_2Me .

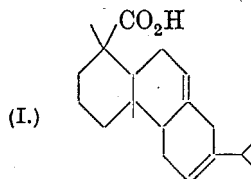
A. LI.

Constituents of higher fungi. I. Triterpene acids of *Polyporus betulinus*. Fr. L. C. CROSS, C. G. ELIOT, I. M. HEILBRON, and E. R. H. JONES (J.C.S., 1940, 632–636).—Extraction of the fresh minced fungus by cold EtOH gives, after saponification, a mixture of sterols containing ergosterol and *polyporenic acid A*, $\text{C}_{30}\text{H}_{48}\text{O}_4$ or $\text{C}_{31}\text{H}_{50}\text{O}_4$, m.p. 194°, $[\alpha]_D^{20} + 69^\circ$ in $\text{C}_5\text{H}_5\text{N}$, which forms a *Me ester*, m.p. 142°, $[\alpha]_D^{20} + 77^\circ$ in CHCl_3 (acetate, m.p. 112°, $[\alpha]_D^{20} + 88^\circ$ in CHCl_3). Further extraction with COMe_2 and Et_2O under reflux affords *polyporenic acid B*, $\text{C}_{30}\text{H}_{48}\text{O}_4$, m.p. 300–310° (decomp.) (after drying in vac., m.p. 275–

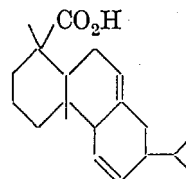
280°) (*Me ester*, m.p. 160°), and *C*, m.p. 270–275° (*Me ester*, m.p. 192–193°), the latter in small amount. Acids *A* and *B* appear to be isomeric, and both contain two OH and two ethylenic linkages. Acid *C* may be identical with gypsogenin.

F. R. S.

Resin acids. II. Structure of abietic acid. V. KRESTINSKI, A. NOVAK, and N. KOMSCHILOV (J. Appl. Chem. Russ., 1939, 12, 1514–1528).—The isomeride (I) of abietic acid, m.p. 170–172°, is ozonised, and the diozonide is decomposed with H_2O at 100°, yielding a mixture of products, of which the following acids were identified: 1 : 3-dimethyl-2-carboxymethyl-3-(δ -keto- ϵ -methyl- α -carboxymethylhexyl)-cyclohexane-1-carboxylic acid, 2-(1'-carboxy-1' : 3'-dimethyl-2'-carboxymethyl-3'-cyclohexyl)-4-isopropyl-cyclohexanone-4 : 5-ozonide, and 1 : 3-dimethyl-2-carboxymethyl-3-($\beta\delta$ -diketo- ϵ -methyl- α -formylmethylhexyl)-cyclohexane-1-carboxylic acid. The isomeride (II) of m.p. 188–190° similarly yields 1 : 3-dimethyl-2-carboxymethyl-3-($\alpha\delta$ -dicarboxy- ϵ -methylhexyl)-cyclohexane-1-carboxylic acid, m.p. 209–213°, 1 : 3-dimethyl-2-carboxymethyl-3-($\gamma\delta$ -dihydroxy- $\alpha\delta$ -dicarboxy- ϵ -methylhexyl)-cyclohexane-1-carboxylic acid (oxidised by KMnO_4 to 1 : 3-dimethyl-3-carboxymethyl- and 3-dicarboxymethyl-cyclohexane-1 : 2-dicarboxylic acid), 1 : 3-dimethyl-2-formylmethyl-3-(α -formyl- δ -carboxy- ϵ -methyl- and -3-($\alpha\delta$ -dicarboxy- ϵ -methyl-hexyl)-cyclohexane-1-carboxylic acid. The production of these acids is explicable on the assumption that the structures of (I) and (II) are :



(I.)



(II.)

R. T.

Miro resin. II. Resin acids. C. W. BRANDT and L. G. NEUBAUER (J.C.S., 1940, 683–686).—Extraction of miro resin with 4% NaOH , followed by saturation with CO_2 , yields *miropinic acid* (I) (85%), $\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. 160°, $[\alpha]_D^{18} - 103.6^\circ$ in 1 : 1 EtOH-CHCl_3 , and *isomiropinic acid* (II), m.p. 284°, $[\alpha]_D^{17} + 21.2^\circ$ in dioxan. (I) forms a *Me ester*, b.p. 148°/0.3 mm., and is hydrogenated (Pd-C) in EtOAc to α -, m.p. 176°, $[\alpha]_D^{18} - 10.5^\circ$ in EtOH , and β -*dihydro-acids*, m.p. 115°, $[\alpha]_D^{18} + 23.2^\circ$ in EtOH . Further hydrogenation in AcOH of the H_2 -acids gives respectively α -, m.p. 170°, $[\alpha]_D^{18} + 15.2^\circ$ in EtOH , and β -*tetrahydro-miropinic acids*, m.p. 170°, $[\alpha]_D^{18} + 30.5^\circ$ in EtOH , along with γ -*dihydromiropinic acid*, m.p. 113°, $[\alpha]_D^{18} + 46.2^\circ$ in EtOH , in both cases. Se-dehydrogenation of (I) yields pimanthrene. Hydrogenation (PtO_2) in AcOH of (II) affords a *resin*, b.p. 200°/0.3 mm. (II) is also obtained by isomerisation of (I) with MeOH-HCl .

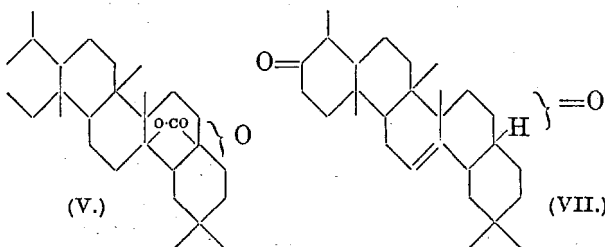
F. R. S.

Colouring matters of the Chinese drug ta-chi, *Euphorbia pikeensis*, Rupr. J. H. CHU (Chinese J. Physiol., 1940, 15, 151–157).—Extraction of the dried root skin with light petroleum gives *euphorbia A*, $\text{C}_{16}\text{H}_{10}\text{O}_5$, m.p. 217° [*Ba salt*, $+1\text{H}_2\text{O}$ and anhyd.; *semicarbazone*, m.p. 287° (decomp.)], converted by Ac_2O and anhyd. NaOAc at 140° into a *compound* $\text{C}_{15}\text{H}_8\text{O}_5$, m.p. 192°, *euphorbia B*, $\text{C}_{15}\text{H}_8\text{O}_5 (+0.5\text{CHCl}_3)$,

m.p. 224°, converted by Ac_2O into a compound, $\text{C}_{14}\text{H}_{11}\text{O}_6$, m.p. 176°, and *euphorbia* C, m.p. 283°. The presence of a glucoside, $\text{C}_{37}\text{H}_{56}\text{O}_{12}$, could not be confirmed. H. W.

Acetyl content of marinobufagin, arenobufagin, and acetylmarinobufagin. V. DEULOFEU, E. DUPRAT, and R. LABRIOLA (*Nature*, 1940, **145**, 671).—Marinobufagin has a volatile acid content <1%; this excludes Ac and EtCO from its constitution. Jensen's formula, $\text{C}_{24}\text{H}_{32}\text{O}_5$, is confirmed. Acetylmarinobufagin (~18% Ac) probably has 2 Ac. A compound, $\text{C}_{24}\text{H}_{32}\text{O}_6$, m.p. 231–233°, Ac <1%, has been isolated from the crude venom of *Bufo arenarum*. L. S. T.

Sapogenins. VII. Structure of quillaic acid and its relation to echinocystic acid. D. F. ELLIOTT, G. A. R. KON, and H. R. SOPER (J.C.S., 1940, 612–617; cf. A., 1939, II, 436).—The second OH of quillaic acid (I), which is not part of the group $\text{CH}(\text{OH})\cdot\text{CMe}\cdot\text{CHO}$, is attached to a C immediately adjacent to the quaternary C carrying CO_2H , as in echinocystic acid (II) (cf. White *et al.*, A., 1939, II, 333). The following reactions suggest that (I) and (II) may be related in the same way as gypsogenin and oleanolic acid. The C_{30} acid (*loc. cit.*) and Kiliani's solution give small amounts of diketolactone (III), acid A_1 (probably $\text{C}_{27}\text{H}_{40}\text{O}_6$) and A_2 , a ketohydroxy-acid, $\text{C}_{29}\text{H}_{44}\text{O}_6$, and acid B, $\text{C}_{31}\text{H}_{48}\text{O}_7$ (*loc. cit.*). The latter, crystallised from aq. MeOH, yields the (?) hydrate (IV), m.p. ~170–180°, which sublimes in high vac. to an unsaturated acid, $\text{C}_{29}\text{H}_{42}\text{O}_5$, corresponding with loss of $\sim\text{AcOH} + \text{H}_2\text{O}$. (IV) and CH_3N_2 afford the Me ester, m.p. 210° [2:4-dinitrophenylhydrazones, m.p. 283° (decomp.)], of acid B, which is decomposed by MeOH-KOH to (IV). (III) and Zn-Hg in HCl-AcOH (cf. Jacobs *et al.*, A., 1926, 1250) yield the keto-lactone (V), m.p. 293–295°. Me quillaate and Cu-bronze at 270°, or Beckmann's



solution in aq. AcOH at 10°, afford the diketolactone (VI), $\text{C}_{30}\text{H}_{44}\text{O}_4$, m.p. 193°, $[\alpha]_D +8.9^\circ$ in CHCl_3 , converted by 5% KOH-EtOH into the diketone (VII), m.p. 197° or m.p. 185° to an opaque liquid which clears at 210°; probably a mixture of stereoisomerides is formed. (VI) and Zn-Hg in AcOH-HCl (method: Reichstein, A., 1937, II, 449, or Jacobs *et al.*, *loc. cit.*) afford the keto-ester, m.p. 178° (formula given), $[\alpha]_D +5.2^\circ$ in CHCl_3 , hydrolysed to a monoketone, $\text{C}_{28}\text{H}_{44}\text{O}$, m.p. 185–187° [CO is no longer inert; 2:4-dinitrophenylhydrazones, m.p. 268° (decomp.)]. Attempts to reduce (Clemmensen) quillaic acid yielded the diacetyl-lactone, which is reduced by Zn-Hg in AcOH-HCl (cf. Jacobs *et al.*, *loc. cit.*) to an isomeride, m.p. 272–274°. Me quillaate (VIII) is reduced

similarly to an impure (?) deoxy-ester. (VIII) and $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HCl}$ in NaOAc-MeOH at room temp. afford a semicarbazone, sintering at 186°, m.p. 200–220°, converted by Na-EtOH at 160–170° into deoxyquillaic acid (IX), m.p. 302° (previous sintering), $[\alpha]_D +34^\circ$ in EtOH. Its Me ester, m.p. 209–210°, is oxidised (method: White *et al.*, *loc. cit.*) to the diketo-ester, $\text{C}_{31}\text{H}_{46}\text{O}_4$, m.p. 152–153° (oxime, m.p. 246–247°). (IX) and its derivatives are probably not identical with, but very similar to, (II) and its derivatives. A. T. P.

Sapogenins. VIII. The sapogenin of fuller's herb. G. A. R. KON and H. R. SOPER (J.C.S., 1940, 617–620).—Saporubin, the saponin of fuller's herb (*Saponaria officinalis*, L.), is hydrolysed by aq. HCl to gypsogenin (I), m.p. 269–270° (previous sintering) [semicarbazone, m.p. 270–272° (decomp.)], also obtained directly from the root (method: Karrer *et al.*, A., 1924, i, 1091). (I) is purified by hydrolysing the acetate (II), m.p. 188–189° (sinters at 173°), $[\alpha]_D +79^\circ$ in CHCl_3 (Me ester, m.p. 191°, $[\alpha]_D +80^\circ$ in CHCl_3), with N-KOH at room temp. to the K salt, thence by dil. HCl to (I), which is sublimed in high vac. at 180°. (II) affords the Br-lactone, m.p. ~180° (decomp.), and isoacetyl-gypsogeninolactone, m.p. 330–332° (cf. Ruzicka *et al.*, A., 1937, II, 201); the latter and $\text{CrO}_3\text{-AcOH-H}_2\text{SO}_4$ yield the corresponding acid, and thence the lactone, $\text{C}_{30}\text{H}_{46}\text{O}_5\cdot\text{H}_2\text{O}$, m.p. 353–355°, of gypsogenic acid (CH_2N_2 affords the Me ester, m.p. 344–345°, of the anhyd. acid). Further oxidation with Kiliani's solution in AcOH affords a monobasic ketonic acid (III), $\text{C}_{29}\text{H}_{44}\text{O}_5$, m.p. ~270–280° (Me ester, m.p. 191–192°; 2:4-dinitrophenylhydrazones, m.p. 246–247°), and hedragone lactone, m.p. 298–301°, clearing at 304° (decomp.) [bromide, m.p. 283° (cf. Kitasato *et al.*, A., 1934, 1223); 2:4-dinitrophenylhydrazones, m.p. 274–276° (decomp.)]. An impure specimen of (I) has probably been obtained from *S. rubra* by von Schulz (cf. A., 1898, i, 204). It is concluded that githagenin from corncockle (cf. Wedekind *et al.*, A., 1930, 1324) is identical with (I); githagonolic acid is probably identical with gypsogenic acid. The formation of githagic acid from githagenin is analogous to the formation of (III) (formulae given). It appears that (I) is a characteristic constituent of saponins in the Caryophyllaceae. A. T. P.

Anomalous Friedel-Crafts reactions. J. A. V. TURCK (Iowa State Coll. J. Sci., 1939, **14**, 98–100).—Alkylation of Et 5-bromo-2-furoate is described again (cf. Gilman and Turck, A., 1939, II, 147, 172). >1 equiv. of AlCl_3 is required for these reactions, and no results are obtained using PhNO_2 , PhCl , or petroleum as solvent. A. Li.

Pyrones and related compounds. I. Formation and structure of 2:6-dihydroxy- γ -pyrone. R. KAUSHAL (J. Indian Chem. Soc., 1940, **17**, 138–143).—Acid-free $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$ (I) (*p*-nitrophenylhydrazones, m.p. 153°) and Ac_2O at <20° give acetonedicarboxylic anhydride (II), m.p. 136–137° (decomp.) (cf. Willstätter *et al.*, A., 1921, i, 92), but at 30° give 2:6-dihydroxy- γ -pyrone (III), m.p. 94°. Warm Ac_2O converts (II) into (III). (III) gives a *p*-nitrophenyl-

hydrazone, m.p. 215° [(II) does not react], and a HgCl_2 compound, m.p. 235°, and is unchanged by hot H_2O or EtOH or cold alkali. Hot alkali decomposes (III). H_2O or EtOH converts (II) into the acid or Et H ester, respectively. With a trace of HCl or H_2SO_4 , (III) gives (I). With PCl_5 (2 mols.) at 100°, (III) gives 2:6-dichloro- γ -pyrone, m.p. 78–80° (hydrochloride, m.p. 105°). With NaOEt-EtOH , (III) gives a Na_2 salt, which with boiling EtI-EtOH gives 2:6-diethoxy- γ -pyrone, b.p. 65–70° [HgCl_2 compound, m.p. 265° (decomp.)], and with $\text{ArCOCl-C}_6\text{H}_6$ yields the di-3:5-dinitrobenzoate, m.p. 90°. PhNCO and (III) give only $\text{CO}(\text{NHP})_2$. AcCl or Ac_2O with a trace of H_2SO_4 converts (III) into dehydroacetocarboxylic acid. With $\text{NH}_3\text{-MeOH}$ at 0°, (II) gives the $(\text{NH}_4)_2$ salt, + MeOH , sinters at 92°, m.p. 97°, of 2:6-dihydroxy-4-pyridone. R. S. C.

Anti-sterility factors (vitamin-E). VII. Red oxidation products of the tocopherols. W. JOHN and W. EMTE (Z. physiol. Chem., 1939, 261, 24–34; cf. A., 1939, II, 175).— α - [absorption max. 270 μ . ($\epsilon < 6800$)] and β -tocopherol-red are obtained from the respective tocopherol by AgNO_3 in boiling EtOH , are reversibly reduced to colourless quinols by $\text{H}_2\text{-Pd}$ -black, and are stable to acid but decomposed by alkali (rate of destruction depends on the solvent). The α -compound gives an oily quinol diacetate [absorption max. 278 μ . (ϵ 1300)]. Chroman-red 141 (I) [prep. by HNO_3 , Ag_2SO_4 , or H_2SO_4 ; AgOAc gives only the quinone, m.p. 79° (best method of prep.); absorption max. 272 μ . (ϵ 5200)] and chroman-red 109 behave similarly; the respective quinol diacetates have m.p. 82° [absorption max. 282 μ . (ϵ 2100)] and 92°. Prep. of (I) by HNO_3 gives also a little (?) 7-hydroxy-2:6-dimethylchroman-5:8-quinone, m.p. 145° [absorption max. 294 μ . (ϵ 22,400)]; quinol diacetate, m.p. 116° [absorption max. 280 μ . (ϵ 630)], but too long oxidation gives a product, $\text{C}_{12}\text{H}_{14}\text{O}_3$, m.p. 129°. These reactions support formulæ previously suggested, but the red substances are bimol., although the quinol diacetates are unimol. R. S. C.

Synthesis of coumarins from o-hydroxyaryl alkyl ketones. D. CHAKRAVARTI and N. DUTTA (J. Indian Chem. Soc., 1940, 17, 65–71; cf. A., 1940, II, 50).—When there is an alkyl substituent in the β -position of the expected cinnamic ester, the coumarin is invariably formed, irrespective of the presence of any α -substituent. Thus 4-alkyl- and 3:4-dialkyl-coumarins are synthesised readily from the respective o-hydroxyaryl alkyl ketones; the presence of halogen or alkyl in the C_6H_5 nucleus of the ketone has little effect. 2:5:1-OH- $\text{C}_6\text{H}_3\text{Cl-COMe}$ and MeI-NaOEt give 5-chloro-2-methoxyacetophenone, b.p. 135°/6 mm., converted by $\text{CH}_3\text{Br-CO}_2\text{Et-Zn}$ wool in C_6H_6 into a OH-ester, and by $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N-Et}_2\text{O}$ into Et 5-chloro-2-methoxy- β -methylcinnamate, b.p. 155°/5 mm., and thence by H_2SO_4 at room temp. or HI (d 1.7) at 140° into 6-chloro-4-methylcoumarin, m.p. 184°. The following aceto- and propio-phenones are prepared from the corresponding Ac and EtCO derivatives of the phenols by AlCl_3 at 130–140° (it is not essential to convert the OH-esters into the unsaturated esters before forming coumarins): 5-bromo-2-methoxy- (I), b.p. 165°/12

mm., 2-methoxy-3-methyl- (II), b.p. 120°/3 mm., and 5-methyl-acetopaenone (III), b.p. 110°/6 mm.: 5-chloro-2-methoxy-3-methyl- (IV), b.p. 139°/8 mm., and 3-chloro-2-methoxy-5-methyl-propiophenone (V), b.p. 140°/8 mm.; 5-chloro-2-methoxy-3-methyl- (VI), b.p. 136°/8 mm., and 4-methyl- (VII), m.p. 81°, and 3-chloro-2-methoxy-5-methyl-acetophenone (VIII), b.p. 124°/4 mm. From (I): Et 5-bromo-2-methoxy- β -methyl-, b.p. 180°/8 mm., and $\alpha\beta$ -dimethyl-cinnamate, b.p. 169–170°/10 mm. (from $\text{CHBrMe-CO}_2\text{Et}$), respectively; from (II): Et 2-methoxy-3: β -dimethyl-cinnamate, b.p. 140–142°/9 mm.; from (III): Et 2-methoxy-5: β -dimethylcinnamate, b.p. 160°/12 mm., and Et β -hydroxy- $\alpha\beta$ -dimethyl- β -(2-methoxy-5-methyl)phenylpropionate, b.p. 140–145°/8 mm.; from (IV): Et 5-chloro-2-methoxy-3: α -dimethyl- β -ethylcinnamate, b.p. 164°/6 mm.; from (V): Et 3-chloro-2-methoxy-5: α -dimethyl- β -ethylcinnamate, b.p. 160°/8 mm.; from (VI): Et 5-chloro-2-methoxy-3: β -dimethyl-, b.p. 163°/5 mm., and $\alpha\beta$ -dimethyl-cinnamate, b.p. 165°/17 mm.; from (VII): Et 5-chloro-2-methoxy-4: β -dimethyl-, b.p. 160°/5 mm., and $\alpha\beta$ -dimethylcinnamate, b.p. 160°/3 mm.; from (VIII): Et 3-chloro-2-methoxy-5: β -dimethyl-, b.p. 160°/6 mm., and $\alpha\beta$ -dimethyl-cinnamate, b.p. 170°/9 mm. From the above are prepared: 6-bromo-4-methyl-, m.p. 187°, and 3:4-dimethyl, m.p. 169°; 4:8-dimethyl-, m.p. 114°, and 4:6-dimethyl-, m.p. 150° (cf. A., 1937, II, 160); 3:4:6-trimethyl-, m.p. 170° (cf. A., 1932, 519); 6-chloro-3:8-dimethyl-4-ethyl-, m.p. 126°; 8-chloro-3:6-dimethyl-4-ethyl-, m.p. 120°; 6-chloro-4:8-dimethyl-, m.p. 155°, and -3:4:8-trimethyl-, new m.p. 114°; 6-chloro-4:7-dimethyl-, m.p. 213°, and -3:4:7-trimethyl-, new m.p. 167°; 8-chloro-4:6-dimethyl-, m.p. 148°, and -3:4:6-trimethyl-coumarin, m.p. 153°, respectively.

A. T. P.

Pechmann condensation of methyl β -resorcylate with some β -ketonic esters. S. M. SETHNA and R. C. SHAH (J. Indian Chem. Soc., 1940, 17, 37–40; cf. A., 1938, II, 452).—Me β -resorcylate and Et α -chloro- or α -benzoyl-acetoacetate, or $\text{CO}(\text{CH}_2\text{-CO}_2\text{Et})_2$, with 80% H_2SO_4 , afford Me 3-chloro-7-hydroxy-4-methyl-, m.p. 218–220° [acetate, m.p. 169–170°; Me ether, m.p. 218–219°; 10% aq. NaOH gives the carboxylic acid (I), m.p. 265–267° (decomp.)], or Me 7-hydroxy-4-phenyl-coumarin-6-carboxylate, m.p. 200–201° (acetate, m.p. 160–161°), + the -carboxylic acid (II), m.p. 285°, or Et 7-hydroxy-6-carbomethoxycoumarin-4-acetate (III), m.p. 194–196° (acetate, m.p. 148–149°), + the -acetic acid (IV), m.p. 184–186° (decomp.), respectively. (I) or (II) is decarboxylated with H_2O at 180–190° to 3-chloro-7-hydroxy-4-methyl-, new m.p. 240°, or 7-hydroxy-4-phenyl-coumarin, m.p. 242–244°, respectively; (IV) at its m.p. until effervescence ceases gives Me 7-hydroxy-4-methylcoumarin-6-carboxylate. (III) and 5% aq. NaOH at 100° (bath) afford 7-hydroxy-4-methylcoumarin-6-carboxylic acid, m.p. 285°. The 4- CO_2Me in the resorcinol nucleus has little retarding influence on the Pechmann condensation. A. T. P.

Kostanecki acylation of oracetophenone. S. M. SETHNA and R. C. SHAH (Current Sci., 1940, 9, 117–118).—A preliminary note.

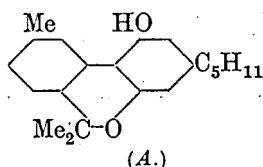
γ -Substituted resorcinol derivatives. III. Synthesis of 5:6-dimethoxyflavone. K. NAKAZAWA (J. Pharm. Soc. Japan, 1939, 59, 194—196).—1:2:6- $C_6H_3Ac(OH)_2$, MeI, and K_2CO_3 in $COMe_2$ yield 6-hydroxy-2-methoxyacetophenone, m.p. 58–5°, converted by oxidation by $K_2S_2O_8$ in alkaline solution and subsequent boiling with dil. H_2SO_4 into 3:6-dihydroxy-2-methoxyacetophenone, m.p. 91°. This is transformed by $BzCl$ in C_6H_5N into the dibenzoate, m.p. 154°, which is converted by $NaNH_2$ in PhMe into 6-hydroxy-3-benzoyloxy-2-methoxydibenzoylmethane, m.p. 152–5°. The diketone is cyclised by conc. H_2SO_4 to 6-hydroxy-5-methoxyflavone, m.p. 185°, methylated (K_2CO_3 and MeI in $COMe_2$) to 5:6-dimethoxyflavone, m.p. 199°. H. W.

Derivatives of 1-, 4-, 6-, and 9-substituted dibenzfurans. J. SWISLOWSKY (Iowa State Coll. J. Sci., 1939, 14, 92—94).—1-Aminodibenzfuran is obtained in 55% yield from the 1-carboxylic acid by a modification of Bywater's method, and in 45% yield from 1-hydroxydibenzfuran by a Bucherer reaction. Nitration of its Ac derivative yields, in Ac_2O at -10° , 2-nitro-1-acetamidodibenzfuran (Gilman *et al.*, A., 1939, II, 276), and in glacial AcOH, the Ac derivative, (I), m.p. 216°, of 4-nitro-1-amino-, m.p. 219—220°, converted by diazotisation and reduction with EtOH into 4-nitro-dibenzfuran, m.p. 120—121°. Catalytic reduction of (I) gives the Ac_1 derivative, m.p. 202°, of 1:4-diaminodibenzfuran, m.p. 86—87° (dihydrochloride, m.p. 322—323°), the Ac_2 derivative, m.p. 307—308°, of which is also prepared from 4-bromo-1-acetamidodibenzfuran. Nitration of (I) and of 2-nitro-1-acetamidodibenzfuran gives 4:7(?)-, m.p. 288°, and 2:6(?)-dinitro-1-acetamidodibenzfuran, m.p. 277—278°, respectively. 1-Bromodibenzfuran with $LiNEt_2$ and $LiNMe_2$ in Et_2O yields respectively 1-diethyl-, m.p. 68—69°, and -dimethyl-aminodibenzfuran, m.p. 98—99°, and with LiBu followed by CO_2 for 10—25 min. (cf. Gilman *et al.*, A., 1939, II, 441) gives the 1-carboxylic acid, bis-1-dibenzfuryl ketone, and a small quantity of tris-1-dibenzfurylcarbinol, m.p. 274—275°, also synthesised from 1-carbomethoxydibenzfuran and Li 1-dibenzfuryl. 3-Acetoxydibenzfuran, m.p. 115—116°, undergoes Fries rearrangement to 3-hydroxy-2-acetyl-, m.p. 168—169° (Me ether, m.p. 113—114°, oxidised to the 3-carboxylic acid), and some 3-hydroxy-4-acetyl-dibenzfuran (Me ether, m.p. 121—122°). 3:6-Dihydroxydibenzfuran (from the Br_2 -compound), m.p. 242—243° (Ac_2 derivative, m.p. 150—151°), yields a Me_2 ether (II), m.p. 88—89° (picrate, m.p. 117—118°), which on mild hydrolysis gives 3-hydroxy-6-methoxydibenzfuran, m.p. 90—91° (Ac derivative, m.p. 110°). Bromination of (II) yields 4:5(?)-, m.p. 196—197°, and 2:7(?)-dibromo-3:6-dimethoxydibenzfuran, m.p. 260—261°. The former with LiBu in C_6H_6 followed by CO_2 gives the 4:5(?)-dicarboxylic acid, m.p. 271—272° [Me_2 ester (CH_3N_2), m.p. 129—130°], also obtained from (II) by direct metalation and carbonation. The latter similarly yields the 2:7(?)-dicarboxylic acid, m.p. 290° [Me_2 ester (MeOH-HCl), m.p. 183—184°], together with some BzOH, formed by the action of LiBu and CO_2 on C_6H_6 . (II) with $(COCl)_2$ and $AlCl_3$ yields a lactone (quinoxaline derivative, m.p. 323—325°), probably

4'-methoxybenzfurano-(1':2':4:5)- or 4'-methoxybenzfurano-(2':1':3:4)-1:2-diketo-1:2-dihydrobenzofuran, which with CH_3N_2 gives Me 3:6-dimethoxy-2(or 4)-dibenzfurylglyoxylate, m.p. 206—207°. Bromination of 3:6-dihydroxydibenzfuran yields the 4:5(?)- Br_2 -compound, m.p. 201—202° (Ac_2 derivative, m.p. 173–5—174°), the Me_2 ether of which (identical with that m.p. 196—197° described above) can be converted into the Me_2 ether, m.p. 106—107°, of 4:5(?)-dimethyl-3:6-dihydroxydibenzfuran, m.p. 168—169°. Attempts to convert this into 4:5-dimethyldibenzfuran via the 3:6-(NH_2) $_2$ -compound were unsuccessful. 3:6-Diaminodibenzfuran (from the Br_2 -compound) has m.p. 212—213° [picrate, m.p. 278° (decomp.)]; the Ac_2 derivative, m.p. 299—300°, on bromination yields 2-bromo-3:6-diacetamido-, m.p. 259—260°, hydrolysed and deaminated to 2-bromodibenzfuran. By the Bucherer reaction, 1:2-dihydroxydibenzfuran yields the hydrochloride, m.p. 275° (darkening at 200°), of 2-amino-1-hydroxydibenzfuran (?) (Ac_2 derivative, m.p. 209—210), whilst 4-bromo-3-hydroxy- yields only 3-amino-dibenzfuran. The (? 5:5)-dibromo-2:2'-dihydroxydiphenyl of Diels and Bibergeil (A., 1902, i, 219) gives a Me_2 ether, m.p. 128—129°, and a Ac_2 derivative, m.p. 105—106°. A. LI.

Cannabis indica. II. Isolation of cannabidiol from Egyptian hashish. Structure of cannabinol. (Miss) A. JACOB and A. R. TODD (J.C.S., 1940, 649—653; cf. A., 1940, II, 185).—Approx. equal amounts of cannabidiol (I), $C_{21}H_{30}O_2$, b.p. 160—180°/0.003 mm., $[\alpha]_D^{25} -126.6^\circ$ in EtOH, and cannabinol (II) (probably A; cf. Cahn, A., 1932, 747) are obtained by distilling the resin from Egyptian hashish. They are purified through their respective *p*-nitrobenzoates, m.p. ~70—80°, and 159—160°. (I) has probably the structure assigned to it by Adams *et al.* (A., 1940, II, 80); its di-3:5-dinitrobenzoate, m.p. 106—107°, $[\alpha]_D^{25} -76.2^\circ$, is identical with that obtained by Adams (from Minnesota wild hemp), and is hydrolysed to (I) by KOH-MeOH in N_2 or by liquid NH_3 . No physiologically active material is isolable from the above resin by alkali extraction. (I) and (II) are inactive in the Gayer test in rabbits. From resin of Indian origin, no (I) has been isolated. (Cf. A., 1940, II, 215.) A. T. P.

Furano-compounds. I. Synthesis of 3'-methyl- or -ethyl-5:6:4':5'-furocoumarin. H. A. SHAH and R. C. SHAH (J. Indian Chem. Soc., 1940, 17, 41—44; cf. A., 1939, II, 373).—5-Hydroxy-6-acetylcoumarin-3-carboxylic acid refluxed with H_2SO_4 -EtOH gives the Et ester, converted by CH_2BrCO_2Et - K_2CO_3 - $COMe_2$ into Et 3-carbethoxy-5-carbethoxymethoxy-6-acetylcoumarin, m.p. 113—115°, hydrolysed by 4% aq. NaOH to 5-carboxymethoxy-6-acetylcoumarin-3-carboxylic acid, m.p. 189—191° (decomp.), which with Ac_2O -NaOAc affords 3'-methyl-5:6:4':5'-furocoumarin-3-carboxylic acid, m.p. 226—228°, and thence (quinoline-Cu-bronze) 3'-methyl-5:6:4':5'-furocoumarin, m.p. 138—140°. Similarly, 5-hydroxy-6-propionylcoumarin-3-carboxylic acid yields the Et



ester, m.p. 152—154°, and thence *Et* 3-carbethoxy-5-carbethoxymethoxy-6-propionylcoumarin, m.p. 103—105°, 5-carboxymethoxy-6-propionylcoumarin-3-carboxylic acid, m.p. 194—196°, 3'-ethyl-5 : 6 : 4' : 5'-furocoumarin-3-carboxylic acid, m.p. 157—158°, and 3'-ethyl-5 : 6 : 4' : 5'-furocoumarin, m.p. 150—152°.

A. T. P.

Constitution of rottlerin. J. N. RAY (Current Sci., 1940, 9, 80).—Contrary to previous observation (A., 1940, II, 139), rottlerin is optically inactive in CHCl_3 . Extraction of *Kamala* (I) with cold Et_2O and adsorption of the extract on Al_2O_3 gives a zone containing isorottlerin (II). Contrary to Robertson *et al.* (A., 1939, II, 559) (II) is not formed during the extraction of (I) by hot PhMe .

H. W.

Mol. wt. of the methyl ether of tetrahydro-rottlerone. J. N. RAY, K. S. NARANG, and B. S. ROY (Current Sci., 1940, 9, 136—137).—The mol. wt. of the Me_2 ether of hydrogenated rottlerone, m.p. 101.5°, is 369.5—372 in C_6H_6 , corresponding with $\text{C}_{20}\text{H}_{20}\text{O}_2(\text{OMe})_2$ contrary to the val. obtained, and the diphenylmethane structure proposed, by McGookin *et al.* (A., 1939, I, 559).

F. R. G.

Pentamethylene oxides and sulphides.—See B., 1940, 346.

Thioxanthenes.—See B., 1940, 433.

Catalytic transformations of heterocyclic compounds. XV. Permanence of activity of the catalyst in the reactions of conversion of furanidin into pyrrolidine or thiophan. J. K. JURIEV and V. A. TRONOVA (J. Gen. Chem. Russ., 1940, 10, 31—34).—Optimum conditions for conducting the reactions (Al_2O_3 catalyst): tetramethylene oxide (I) + $\text{NH}_3 \rightarrow$ pyrrolidine; (I) + $\text{H}_2\text{S} \rightarrow$ tetramethylene sulphide; furan + $\text{H}_2\text{S} \rightarrow$ thiophen, are described; the optimum temp. is 400°, in all cases. The catalyst does not suffer inactivation.

R. T.

Physiologically-active stimulants in foods and their detection. W. DIEMAIR (Atti X. Congr. Internaz. Chim., 1938, IV, 497—517).—See A., 1940, III, 592. N^α -Benzoylhistidine Me ester (I) (Gerngross, A., 1921, i, 57) coupled with PhN_2Cl (accompanied by spontaneous de-esterification) yields 2 : 5-di-benzeneazo- N^α -benzoylhistidine, m.p. 145.5° (*Me* ester, m.p. 217°), whilst coupling with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ affords 2 : 5-di- p -nitrobenzeneazo- N^α -benzoylhistidine, m.p. 161—162°; N^α -benzoylhistamine with PhN_2Cl yields only 5-benzeneazo- N^α -benzoylhistamine, m.p. 186.5° (decomp.). Glyoxaline with $\text{NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ gives 2- p -nitrobenzeneazoglyoxaline, m.p. 248°. With I (I) yields 2-iodo- N^α -benzoylhistidine *Me* ester, m.p. 189° (all m.p. uncorr.). The bearing of the formation and properties of these derivatives on the Pauly diazo-reaction is discussed.

F. O. H.

3 : 3-Dimethylthiolindoline.—See B., 1940, 383.

β -Indolylacetic acids.—See B., 1940, 346.

***Coli*-tryptophan-indole reaction. III. Essential structural conditions for the enzymic degradation of tryptophan to indole.** J. W. BAKER and F. C. HAPPOLD (Biochem. J., 1940, 34, 657—663).—The breakdown of tryptophans to indoles by *E. coli* appears to require, *inter alia*, a free CO_2H , an un-

substituted $\alpha\text{-NH}_2$, and a $\beta\text{-C}$ capable of oxidative attack. The following appear new : *l*- p -nitrobenzoyl-tryptophan, m.p. 121° (decomp.) after softening at 114° (possibly + 1EtOH); *Me* *l*- α -methylamino- β -3-indolylpropionate hydriodide, m.p. 192°; 3-indolylacetamide, m.p. 150—151°, by heating NH_4 3-indolylacetate with $(\text{NH}_4)_2\text{CO}_3$ at 200—210°; indole-3-aldehydesemicarbazone, m.p. 220° (decomp.). It is doubtful if *l*-tryptophan reacts simply with CH_2O .

H. W.

Phenylpyridines.—See B., 1940, 346.

Benzacridones.—See B., 1940, 433.

Carcinogenic compounds. I. Synthesis of 9-azacholanthrene and of certain meso-alkyl derivatives of 1 : 2- and 3 : 4-benzacridine. I. J. POSTOVSKI and B. N. LUNDIN (J. Gen. Chem. Russ., 1940, 10, 71—76).— $m\text{-NH}_2\text{-C}_6\text{H}_4\text{[CH}_2\text{]}_2\text{CO}_2\text{H}$ and $\alpha\text{-C}_{10}\text{H}_7\text{-OH}$ heated with ZnCl_2 (5 hr. at 280—290°) yield 9-azacholanthrene, m.p. 187—188° [*picrate*, m.p. 222—224° (decomp.)]. $\alpha\text{-C}_{10}\text{H}_7\text{-NHPh}$ and AcOH or EtCO_2H heated with ZnCl_2 (14 hr. at 230—240°), afford 5-methyl-, m.p. 126° [*hydrochloride*, m.p. 253°; *picrate*, m.p. 231° (decomp.)], or 5-ethyl-1 : 2-benzacridine, m.p. 123° [*hydrochloride*, m.p. 250°; *picrate*, m.p. 227° (decomp.)]. 5-Methyl-, m.p. 144° [*hydrochloride*, m.p. 266°; *picrate*, m.p. 239° (decomp.)], and 5-ethyl-3 : 4-benzacridine, m.p. 139°, are prepared similarly from $\beta\text{-C}_{10}\text{H}_7\text{-NHPh}$.

R. T.

Stabilised diazo-complexes with piperazine and other bases. P. J. DRUMM, W. F. O'CONNOR, and J. REILLY (Sci. Proc. Roy. Dublin Soc., 1940, 22, 223—227).—Diazonium salts with piperazine and with NHMe-OH give stable complexes which reproduce the diazonium salts in 55—98% yield when heated to 45° with 80% H_2SO_4 . *Bis*-3-, m.p. 160.5° [reduced ($\text{Zn} + \text{EtOH-AcOH}$) to NN' -diaminopiperazine], and -4-chloro-6-methyl-, m.p. 184°, and -2 : 5-dichloro-benzeneazopiperazine, m.p. 146°, and -3-, m.p. 76°, and 4-chloro-6-methyl-, m.p. 84°, and 2 : 5-dichloro-benzeneazo- β -methylhydroxylamine, m.p. 112°, are described.

A. LI.

Bisisoindolenylidenes.—See B., 1940, 349, 434.

Reaction of unsaturated halogen compounds of the types $\text{CR}_2\text{:CX}_2$ and NR:CX_2 with azides. I. Reaction of phenylcarbylamine chloride with sodium azide. P. S. PELKIS and C. S. DUNAIEVSKAJA (Mem. Inst. Chem. Ukrain. Acad. Sci., 1940, 6, 163—180).— NPh:CCl_2 and NaN_3 in COMe_2 (at the b.p.) yield 5-azido-1-phenyl-1 : 2 : 3 : 4-tetrazole.

R. T.

Magnetochemical investigations. XXXV. Heavy-metal complexes of phthalocyanine. H. SENFF and W. KLEMM (J. pr. Chem., 1940, [ii], 154, 73—81).—The magnetic susceptibilities of the phthalocyanine complexes of Ni, Co, Fe, and Mn indicate a transition from penetration to normal complex in this series. In the V complex the metal is quadrivalent. The $\text{C}_5\text{H}_5\text{N}$ and quinoline compounds of the Fe complex are diamagnetic.

J. W. S.

Acylamidomorpholines.—See B., 1940, 431.

Biogenesis of vitamin-B₁. C. R. HARRINGTON and R. C. G. MOGGRIDGE (Biochem. J., 1940, 34,

685—689).—The action of pressed top yeast on α -amino- β -(4-methylthiazole-5)-propionic acid (I) and sucrose in H_2O gives 4-methyl-5- β -hydroxyethylthiazole [picrate, m.p. 162° ; picrolonate, m.p. 184° (decomp.); *p*-nitrobenzoate, m.p. 125°] and d(—)- α -amino- β -(4-methylthiazole-5)-propionic acid, $[\alpha]_D -9.0^\circ$ in $N-H_2SO_4$, which appears homogeneous and gives a strongly positive ninhydrin reaction. The *Me* ester hydrochloride, m.p. 187° (decomp.), does not appear to react with NH_4Et_2 , $ClCO_2CH_2Ph$, or $AcCl$. 4-Methylthiazole-5-aldehyde and acetyl glycine yield the azlactone,
$$\begin{array}{c} \text{CH-S} \\ \diagup \quad \diagdown \\ \text{N-CMe} \gg \text{C-CH:C} \ll \text{CO-O} \\ \diagdown \quad \diagup \\ \text{N=CMe} \end{array} \quad \text{m.p. } 157.5^\circ$$
 converted by $NaOMe-MeOH$ into *Me* α -acetamido- β -(4-methylthiazole-5)-acrylate, m.p. 160° . α -Acetamido- β -(4-ethylthiazole-5)-propionic acid has m.p. 191° . Attempts to condense 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide (II) with (I) were unsuccessful. α -Acetamido- β -(4-methylthiazole-5)-propionic acid and (II) at 160° afford the acid,
$$\text{CMe} \begin{array}{c} \diagup \text{N:C(NH}_2\text{, HBr)} \\ \diagdown \text{N} \end{array} \text{---CH} \gg \text{C-CH}_2\text{.NBr} \begin{array}{c} \text{CH-S} \\ \diagup \quad \diagdown \\ \text{CMe.C-CH}_2\text{.CH} \end{array} \begin{array}{c} \text{NHAc} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{H} \end{array}$$
 decomp. 260° , hydrolysed by HBr to the NH_2 -acid [tripicrate, m.p. 164° (decomp.); tribromide, m.p. 233° (decomp.)]. H. W.

Synthesis of heterocyclic derivatives of sulph-anilamide. K. GANAPATHI and B. K. NANDI (Current Sci., 1940, **9**, 67—68).—5-Amino- and 2 : 8-diamino-acridine, 2-sulphanilamidopyridine, and 2-aminothiazole are condensed with *p*-NHAc·C₆H₄·SO₂Cl in COMe₂ or C₆H₅N and the products are hydrolysed (2·5N-NaOH or 4—5N-HCl) to 5-sulphanilamido- and 2 : 8-disulphanilamidocridine, 2-*p*-sulphanilamidobenzenesulphonamidopyridine, and 2-sulphanilamidothiazole respectively.

Heterocyclic and other derivatives of sulphanilamide. B. K. NANDI and K. GANAPATHI (Current Sci., 1940, **9**, 177; cf. preceding abstract).—Condensation of $p\text{-NHAc-C}_6\text{H}_4\text{-SO}_2\text{Cl}$ with the appropriate NH_2 -compounds in COMe_2 or $\text{C}_5\text{H}_5\text{N}$, followed by hydrolysis with NaOH or HCl , yields 2-N'-sulphanilamido-4-methylthiazole, -4-phenylthiazole, -anthraquinone, and -5-hydroxy-1 : 3 : 4-thiodia-
A. LI.

Strychnine and brucine. III. Derivatives of dinitrostrychnic acid. R. H. SIDDIQUI (Proc. Indian Acad. Sci., 1940, **11**, A, 268—281).—Dinitrostrychnic acid nitrate (I) (the dinitrostrychnine hydrate nitrate of Tafel, A., 1898, i, 706) and $\text{MeOH} \cdot \text{H}_2\text{SO}_4$ afford, through the *sulphate* (+MeOH) of (II), *Me dinitrostrychnate* (II), m.p. 210—211° (decomp.) (+MeOH, lost at 110° in vac.) [*hydriodide*, +MeOH (not lost at 140°), m.p. 245—246° (decomp.); hydrochloride, + H_2O , m.p. 245—247° (decomp.); picrate, chars at 275°; *methiodide* (III), + H_2O , m.p. 240—242° (decomp.) (shrinks at 215°)]. (III) and AgOH afford N(b)-*methyldinitrostrychnic betaine*, m.p. >310° [*picrate*, m.p. 276—277° (decomp.) (browns at 265°)]. (II) refluxed with piperidine affords dinitrostrychnic acid (IV), +1.5 H_2O . *Et*, m.p. 226° (decomp.) [*sulphate*, +1.5EtOH; *hydrochloride*, + H_2O , m.p. 230° (decomp.) (softens at 190°); *picrate*], and *Pr dinitrostrychnate*, m.p. 246—247° (decomp.) [*sulphate*,

m.p. 210°; *hydrochloride*, +H₂O, m.p. 230° (decomp.); picrate, chars from 254°, are prepared. (II) and SnCl₂-HCl or Zn-HCl afford diaminostrychnine (V), new m.p. 287° (decomp.), also obtained from (IV). (II) and N₂H₄.H₂O in Bu⁺OH give *dinitrostrychnic acid hydrazide (dihydrochloride, +H₂O; picrate; sulphate; perchlorate)*, converted by NaNO₂-AcOH at 7° and then boiling EtOH into a *substance*, C₂₁H₂₂O₆N₄, +0.5H₂O, m.p. 265° (softens at 175°, froths at 198°) (*hydrochloride, +0.5H₂O*), a *substance*, C₂₁H₂₃O₆N₅.H₂O, m.p. >320° [(?) amide of (IV)] (*hydrochloride*), and a *substance*, C₂₁H₂₂O₆N₄.H₂O, decomp. from 240° [(?) aldehyde related to (IV)] (*hydrochloride, +H₂O*). (IV) and aq. KOH yield an (?) isomeride (VI) [*hydrochloride, C₂₁H₂₂O₇N₄.HCl; Me ester (VII), m.p. 165° (decomp.), then, after recrystallisation, 209°; cf. (II)]*. (I) or (VI) and Ac₂O-NaOAc at 100° afford (after MeOH) (VII) and a *base*, decomp. from 235—248° (softens at 233°), probably α -dinitrostrychnine, converted by Bu⁺OH-H₂O into (?) (IV), reduced to (V). (I) and HNO₃ (*d* 1.42) afford H₂C₂O₄, picric acid, dinitrostrychnol-dicarboxylic acid (cf. Ashley *et al.*, A., 1930, 625), an *acid*, C₃₈H₆O₇N₂, m.p. 182° (softens at 175°), two acids, m.p. 230—235° and 195°, respectively, and a K salt, m.p. 220°. The structure of strychnine is discussed.

A. T. P.

Strychnine and brucine. IV. isoStrychnic acid. R. H. SIDDIQUI (J. Indian Chem. Soc., 1940, 17, 152—156; cf. preceding abstract).—*isoStrychnic acid* (I), $C_{21}H_{24}O_3N_2$, m.p. 240° (A., 1907, 1208, 231°), contains 1 mol. of H_2O of crystallisation, of which 0.5 mol. is lost at 135°/vac., gives a *hydrochloride*, $+H_2O$, m.p. 190—195° (decomp.), *picrate*, m.p. 187—189° (decomp. from 130°), and by Ac_2O at 100° an *O-Ac* derivative, $+2H_2O$ (lost at 100°/vac.), m.p. 195—196° (decomp.) [*hydrochloride*, m.p. 225—226°; *picrate*, m.p. 184° (decomp.)], and with $BzCl-C_6H_5N$ gives $BzOH$ and *isostrychnine*. It is unaffected by hot 5—10% HNO_3 , with 20% HNO_3 gives an amorphous powder, but with boiling 50% HNO_3 gives *dinitroisostrychnic acid*, $C_{21}H_{22}O_7N_4$, $+1.5H_2O$, m.p. $>325^\circ$ (*hydrochloride*; *sulphate*; resists reduction), and an amorphous acid, m.p. 260—271°. The structure of (I) is discussed. R. S. C.

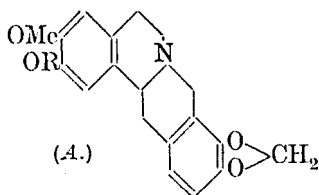
R. S. C.

Strychnine and brucine. V. Derivatives of dinitroisostrychnic acid. R. H. SIDDIQUI (J. Indian Chem. Soc., 1940, **17**, 233—238).—The *Me* ester, m.p. 225° (softens at 218°) [*sulphate*, chars at 280—290°; *hydrochloride*, softens at 194° and chars at 225—235°; *picrate*, m.p. 259° (decomp.)], of dinitroisostrychnic acid (I) with MeI in CHCl₃ yields the *methiodide*, m.p. 276—280° (decomp.), which with Ag₂O gives the *betaine*, m.p. <325° (*picrate*, decomp. 259°). The Et ester, m.p. 195° (softening at 192°) [*sulphate*, decomp. 250° (frothing at 150°); *hydrochloride*, decomp. 247°; *picrate*, m.p. 261° (decomp.)], of (I) is not affected by piperidine, and yields, with HNO₂, the *nitrile*, m.p. 198—199°, with Br in CHCl₃, a *Br*-derivative, m.p. 180°, and with N₂H₄·H₂O in BuOH, a mixture of the *hydrazide* (+0.25H₂O), m.p. <280°, with two *substances*, C₂₁H₂₃O₆N₅·H₂O, m.p. 221° [*picrate*, m.p. 225—235° (frothing)], and C₂₁H₂₃O₅N₅·0.25H₂O, m.p. 160° (frothing) [*picrate*,

m.p. 225—235° (frothing at 178°)]. The *Pr* ester of (I) has m.p. 118—122° [sulphate, m.p. 247—248° (decomp.); hydrochloride, m.p. 225° (frothing); picrate, m.p. 241—244° (decomp.)]. A. Li.

Alkaloids of fumariaceous plants. XXVI. *Corydalis claviculata* (L.), DC. XXVII. A new alkaloid, cheilanthifoline, and its constitution. R. H. F. MANSKE (Canad. J. Res., 1940, 18, B, 97—99, 100—102).—XXVI. *C. claviculata* (L.), DC., contains cularine (I), suggesting the lack of any close relationship to *C. hutea* and *ochroleuca* (cf. A., 1939, II, 395). Protopine, partly racemised *l*-stylopine, and a phenolic base or mixture of bases, alkaloid F52, methylated to (I), are also present.

XXVII. *Cheilanthifoline* (alkaloid F13) (II), m.p. 184°, $[\alpha]_D^{20}$ -311° in MeOH, obtained from *C. cheilanthifolia*, and in smaller amounts from *C. scouleri* and *C. siberica* (A., 1937, II, 265), has the structure (A; R = H). With CH₂N₂ in MeOH (II) gives sinactine (III) (A; R = Me). With CHMeN₂ in MeOH-Et₂O, (II) gives its *O*-Et ether, m.p. 144°, which is oxidised by KMnO₄-Na₂CO₃ to 1-keto-6-methoxy-7-ethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline (cf. Gadamer *et al.*, A., 1928, 310) and 4-methoxy-5-ethoxyphthalic acid. The identity of alkaloid F36 from *Fumaria officinalis* (A., 1939, II, 190) with partly racemic (III) is confirmed. E. W. W.



Salts of rubradinine. P. DENIS (Bull. Acad. roy. Belg., 1939, [v], 25, 177—182; cf. A., 1937, II, 266).—Rubradinine contains 1 OMe and its formula is therefore C₂₃H₂₅O₃N₂·OMe. The non-cryst. hydrochloride, sulphate, C₂₄H₂₈O₄N₂·H₂SO₄·5H₂O, m.p. 245° (block), *per*-rhenate, *platinichloride*, *aurichloride*, and *mercurichloride* are described. H. W.

Synthesis of lipophilic chemotherapeutics. II. 4-Alkylaminoazobenzene-4'-arsonic acids. S. ADLER, L. HASKELBERG, and F. BERGMANN (J.C.S., 1940, 576—578).—A series of dyes, R·NH·C₆H₄·N=N·C₆H₄·AsO₃H₂, has been prepared by coupling diazotised *p*-arsanilic acid with a solution of the substituted NH₂Ph, usually in AcOH. The lower members of the series are very toxic, the higher ones show a definite decrease in toxicity. The following are described: *sec*.-butyl-, b.p. 225°/759 mm., *sec*.-butylcarbinyl-, b.p. 236°/758 mm., *β*-methylamyl-, b.p. 138°/22 mm., *dodecyl*-, b.p. 140°/0.2 mm., *tetradecyl*-, b.p. 180°/4 mm., and *octadecylaniline*, b.p. 196°/0.6 mm., and 4-dimethyl-, m.p. 310° (decomp.), *ethyl*-, m.p. 276° (decomp.), *n*-propyl-, m.p. 286° (decomp.), *n*-butyl-, *isobutyl*-, m.p. 303° (decomp.), *sec*.-butyl- (+EtOH), *n*-amyl-, *sec*.-butylcarbinyl-, m.p. 245° (decomp.), *n*-hexyl-, m.p. 270° (decomp.), *β*-methylamyl-, m.p. 265° (decomp.), *n*-heptyl-, *n*-dodecyl-, *n*-tetradecyl-, *n*-octadecyl-, *cyclohexyl*-, m.p. 292° (decomp.), *benzyl*-, m.p. 340° (decomp.), and *cholesteryl-aminoazobenzene-4'-arsinic acid*, m.p. 237° (decomp.). F. R. S.

Mercuration of some simple derivatives of

***γ*-pyrone.** J. R. FILES and F. CHALLENGER (J.C.S., 1940, 663—670).—*γ*-Pyrone with Hg(OAc)₂ in H₂O-AcOH at 100° followed by HCl gives *dichloromercuri-γ-pyrone*. Dimethylpyrone with HgCl₂ and NaOAc affords a *trichloromercuri-derivative*. Meconic acid, NaOAc, and HgCl₂ yield *hydroxymercuricomenic anhydride*, CO₂, and Hg₂Cl₂; the pure anhydride is obtained by using HgO. This substance and HCl give *chloromercuricomenic acid*, which with Br affords 2-bromocomenic acid. Mercuration of comenic acid with Hg(OAc)₂ or HgCl₂ and NaOAc leads to the anhydride. Pyromeconic acid and HgCl₂ with NaHCO₃-glycerol give the anhydride of *hydroxymercuripyromeconic acid*, which with HCl forms *monochloromercuripyromeconic acid* (I); the acid with HgCl₂ and NaOAc yields *oxymmercurichlorochloromercuripyromeconic acid*, which with HCl affords *dichloromercuripyromeconic acid*. With (I) and I, iodopyromeconic acid, with I in position 2, is obtained. Kojic acid with HgCl-NaOAc or NaHCO₃-glycerol gives *hydroxymercurikojic anhydride*, which with Me forms *chloromercurikojic acid*; treatment with Na₂S and NaI results in elimination of Hg. Almost all these mercurated products are amorphous, insol., infusible solids. F. R. S.

Organo-mercury compounds derived from quinine and cinchonine. N. V. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1940, 11, A, 289—297).—Quinine (I) (1 mol.) and HgCl₂ (1 mol.) in cold EtOH afford *quinine-monomercuri chloride* (II), m.p. ~140—170°; 2 or more mols. of HgCl₂ give the *dimmercuri chloride* (III), m.p. ~130—160°. (I) in H₂O, +HCl until just acid, and cold aq. HgCl₂ (1 or 2 mols.) afford the *monohydrochloride monomercuri chloride* (IV), m.p. 204° (chars); in hot aq. HCl, the *dihydrochloride monomercuri chloride* (V), m.p. 255° (decomp.), is formed. (V) and cold 10% aq. NaOH give (IV). (II), (III), or (IV) and boiling dil. HCl give (V). Hg is retained in solution as stable complex ions, probably of type K⁺(HgCl₃)' or K₂⁺⁺(HgCl₄)'', when (IV) or (V) is boiled with aq. KOH. (I) and aq. Hg(OAc)₂-AcOH-aq. NaOH afford *α-hydroxymercuri-β-hydroxydihydroquinine*, +2H₂O, decomp. 115° (freshly prepared) or 166° (dried in air), converted by AcOH into *α-acetoxymmercuri-β-hydroxydihydroquinine acetate* (VI), +2H₂O. Cinchonine affords, as above, a *monomercuri*, m.p. 172° (decomp.) and *dimmercuri chloride* (from 3 mols. of HgCl₂), m.p. 155—172°, a *mono*-, m.p. 120—166°, and *dihydrochloride monomercuri chloride*, m.p. ~95—128° (decomp.) (+3H₂O, lost at 100°), and *α-hydroxymercuri-β-hydroxydihydrocinchonine*, +H₂O, m.p. 235° (turns brown at 212°) (acetate). Formulae are proposed for (II), (V), and (VI). A. T. P.

Organometallic compounds of group VIII elements. M. LICHTENWALTER (Iowa State Coll. J. Sci., 1939, 14, 57—59; cf. Gilman *et al.*, A., 1939, II, 53, 253).—Of the group VIII metals, only Pt could be made to yield organometallic compounds. Fe, Co, and Ni do not combine directly with org. halides. MgPhI with Fe, Co, or Ni halides (except FeF₃) in Et₂O-C₆H₆ gives the metal and Ph₂ in 100% yield. FeCl₂ or FeI₂ with α-C₁₀H₇-MgBr or α-C₁₀H₇-Li yields some (1-C₁₀H₇)₂; addition of CH₂PhBr before hydrolysis

gives no ketone. FeI_2 slowly yields Ph_2 with ZnPhCl , and a mixture of C_2H_4 , C_2H_6 , and C_4H_{10} with ZnEtI . PbEt_4 rapidly reduces FeCl_3 to FeCl_2 . FeI_2 (with or without Fe powder) with $\text{Pb}(\text{C}_6\text{H}_4\cdot\text{OMe-}p)_3$ in $\text{Et}_2\text{O-C}_6\text{H}_6$ ppts. PbI_2 and $\text{Pb}(\text{C}_6\text{H}_4\cdot\text{OMe-}p)_4$; hydrolysis of the solution gives chiefly $\text{PbI}_2(\text{C}_6\text{H}_4\cdot\text{OMe-}p)_2$. PtCl_4 with MgPhI gives an amorphous mixture of Ph-Pt compounds containing 30–40% of Pt. PtCl_2 with MgMeI gives an amorphous substance analysing correctly for PtMe_3I_2 , and with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ gives *Pt di- α -naphthyl*, in presence of which (as of PtCl_4) BzBr and *m*-xylene give a 70–80% yield of 2:4:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{COPh}$. Anhyd. PtCl_4 with MgMeI yields PtMe_3I (40%), together with a trace of PtMe_3 , and compounds having compositions corresponding with PtMeI_5 , PtMe_3I , and PtMeI_3 . A. LI.

Organometallic radicals. J. C. BAILIE (Iowa State Coll. J. Sci., 1939, 14, 8–10).—Some Pb triaryls are described again (cf. Gilman and Bailie, A., 1939, II, 233). *Pb tri-*p*-phenethylbenzyl* [from $\text{PbNa}(\text{C}_6\text{H}_4\cdot\text{OEt-}p)_3$ and CH_2PhCl] has m.p. 76–77°. When $\text{R} = \text{Ph}$, *p*-tolyl, *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$, *p*- $\text{C}_6\text{H}_4\cdot\text{OEt}$, or Et : $2\text{PbR}_3 + \text{MgI}_2 + \text{Mg} \rightarrow \text{PbR}_4 + \text{Pb} + 2\text{MgRI}$, probably with the intermediate formation of $\text{PbR}_3\cdot\text{MgI}$; the *o*-substituted Pb triaryls with MgI_2 and Mg yield PbR_3I , whilst PbPh_4 and $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}p)_3$ do not react. PbPh_3 or $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}p)_3$ with MgI_2 alone yields PbR_3I . PbR_3Na ($\text{R} = \text{aryl or alkyl}$) with NH_4X in liquid NH_3 yields PbR_3 and Pb , the colour changes indicating that the reaction is probably $\text{PbR}_3\text{Na} \rightarrow \text{PbR}_3\text{H} \rightarrow \text{PbR}_3 + \text{RH}$; $3\text{PbR}_3 \rightarrow 2\text{PbR}_3 + \text{Pb}$. PbPh_3Cl , PbPh_3Br , or PbPh_3I with $\text{CPh}_3\cdot\text{MgCl}$ affords *Pb triphenyltriphenylmethyl* (?) (I), m.p. 196–197°, which in C_6H_6 dissociates appreciably, and is slowly oxidised to PbPh_3 and $(\text{CPh}_3)_2\text{O}_2$. The following reactions of (I) are recorded: thermal decomp. in xylene gives PbPh_4 and Pb ; the reaction with $\text{HCl} + \text{I}$ is inconclusive, but dry HCl yields, in CHCl_3 , $\text{CPh}_3\cdot\text{OH}$, and in light petroleum (b.p. 60–66°), PbPh_2Cl_2 ; I in CHCl_3 gives PbI_2 and a trace of PbPh_3I ; Na in liquid NH_3 gives a mixture of CPh_3Na and PbPh_3Na , which yields with NH_4Br , CHPh_3 and PbPh_3 , and with CH_2PhCl , $\text{CPh}_3\cdot\text{CH}_2\text{Ph}$ and $\text{PbPh}_3\cdot\text{CH}_2\text{Ph}$. (I) could not be prepared by mixing CPh_3 and PbPh_3 . *Sn triphenyltriphenylmethyl*, m.p. 272–273° (decomp.) (from SnPh_3Cl and $\text{CPh}_3\cdot\text{MgCl}$), does not dissociate in C_6H_6 . With Na followed by NH_4Br in liquid NH_3 it yields CHPh_3 and SnPh_3 ; the comparatively slow reaction with HCl to give *Sn diphenyltriphenylmethyl chloride*, m.p. 210°, shows that the C-Sn bond is more stable than the C-Pb. $\text{PbI}(\text{C}_6\text{H}_4\cdot\text{OMe-}o)_3$ and $\text{CPh}_3\cdot\text{MgCl}$ yield *Pb tri-*o*-anisyltriphenylmethyl*, m.p. 145–146°. $\text{CPh}_3\cdot\text{MgCl}$ with PbCl_2 in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ gives CPh_3 and Pb . A. LI.

Acridine derivatives. V. Aurothiol- and argentothiol-acridines. S. J. DAS-GUPTA (J. Indian Chem. Soc., 1940, 17, 244–246).—5-Thiolacridines exist in two forms (? thio-ketonic and -enolic), one form yielding the other when dissolved in alkali and reprecipitated by acid. 7-Methoxy-5-thiolacridine, m.p. 231–232° (from the 5-chloroacridine and K xanthate in PhOH), in EtOH yields, with SO_2 followed by KAuBr_4 , the 5-aurothiolacridine, m.p. 219–220°

(decomp.), with KAuBr_4 followed by SO_2 , bis-7-methoxy-5-acridylthiolgold bromide, m.p. 222–223°, and with NaOH followed by AgNO_3 , 7-methoxy-5-argentothiolacridine, m.p. 261° (decomp.). The corresponding compounds from 2-chloro-7-methoxy-5-thiolacridine, m.p. 245°, have m.p. 247–248° (decomp.), 254–255° (decomp.), and 290° (decomp.), respectively.

A. LI.

Structure of proteins. A. OLSEN (Tids. Kjem., 1940, 20, 45–52).—A review. M. H. M. A.

Cyclol hypothesis. D. WRINCH (Nature, 1940, 145, 669–670).—Experiments cited as evidence against the hypothesis are accommodated with it.

L. S. T.

Number and range of dissociation of ionogenic groups and the dissociation curve of proteins. I. LICHTENSTEIN (Biochem. Z., 1939, 303, 13–31).—Acid- and base-binding capacities of gelatin, deaminated gelatin, and crust. egg-albumin have been determined between pH 1.5 and 12.5 in H_2O , in 80% EtOH , and in 1% CH_2O , and the curves obtained are compared with those derived from data on the constituent NH_2 -acids and on the proportions of these in the respective proteins. The dissociation range of all single groups, and the no. of NH_2 and glyoxaline groups (corresponding respectively with the lysine and histidine content of gelatin), are in agreement with available analytical data, but the no. of free CO_2H is approx. twice that to be expected from the accepted content of dibasic NH_2 -acids. A discrepancy also exists with regard to guanidino-groups calc. on the basis of the arginine content. Correct isoelectric points can be calc. from dissociation ranges and nos. of groups derived from the titration curves, but not from analytical data. F. L. U.

Simplified micro-determination of carbon and hydrogen in organic compounds. I. Combustion of compounds containing carbon, hydrogen, and oxygen. II. (FRLN.) A. DOMBROWSKI (Mikrochem., 1940, 28, 125–135, 136–140).—I. Org. substances are burnt in O_2 in a shortened Pregl combustion tube using only Cu gauze therein. Shortened absorption tubes are more convenient.

II. With the above-mentioned apparatus, N oxides are absorbed in a tube, containing *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ and aq. $\text{H}_3\text{BO}_3\text{-K}_2\text{Cr}_2\text{O}_7$, placed between the H_2O - and CO_2 -absorption tubes. S and halogen are absorbed by Ag (followed by CuO , PbCrO_4 , and finally Ag). R. S. C.

Systematic qualitative organic micro-analysis.—See A., 1940, I, 301.

Semi-micro-Dumas method for difficult compounds. A. R. RONZIO (Ind. Eng. Chem. [Anal.], 1940, 12, 303–304).—The method previously described (A., 1936, 578) is modified by using pptd. MnO_2 in the combustion tube, which burns CH_4 quantitatively to CO_2 . A special nitrometer is described. J. D. R.

Bomb determination of organic chlorine by lime-fusion method. W. M. MACNEVIN and W. H. BAXLEY (Ind. Eng. Chem. [Anal.], 1940, 12, 299–300).—A suitable bomb is described. The use of a sealed metal tube makes the process available

for volatile liquids, and is quicker than the Carius method. Procedure is detailed. J. D. R.

Determination of organic iodine by the micro-method of Leipert. A. BONOT (Bull. Soc. Chim. biol., 1940, 22, 108—111).—Conditions to be observed for the determination of 0.1—1 mg. of I are described. A. L.

Determination of methylpropene by a modified Denigès reagent. A. NEWTON and E. J. BUCKLER (Ind. Eng. Chem. [Anal.], 1940, 12, 251—254).—The normal determination of CMe_2CH_2 by the Denigès reagent $[\text{Hg}(\text{NO}_3)_2\text{--HNO}_3]$ is complicated by the solubility of the ppt. in HNO_3 and by changes in its wt. and composition on washing with H_2O . Use of a neutralised reagent and determination of the Hg in the ppt. (not the wt. of the ppt.), which is const. under the conditions of determination $[7\text{Hg} \equiv \text{CMe}_2\text{CH}_2]$, gives an accurate and rapid determination. C_2H_4 , C_3H_6 , Δ^{γ} -butadiene, Δ^{α} - and Δ^{β} -butene, and β -methyl- Δ^{β} -butene do not interfere. Apparatus and procedure are detailed. J. D. R.

Equivalent weights of salts of organic acids. Micro-determination by electrodialysis. K. H. DITTMER and R. G. GUSTAVSON (Ind. Eng. Chem. [Anal.], 1940, 12, 297—299).—The aq. salt solution is electrodialysed through a sintered glass membrane, the metal forming an amalgam with the Hg cathode and thence combining with a known excess of standard H_2SO_4 in the cathode vessel. Titration of the cathode acid after electrodialysis gives the equiv. wt. of the acid. Apparatus and procedure are detailed, and methods are described for prep. of sintered glass membranes. The error is $\pm 3\%$. J. D. R.

Quantitative analysis by isotope dilution, with application to the determination of amino-acids and fatty acids. D. RITTENBERG and G. L. FOSTER (J. Biol. Chem., 1940, 133, 737—744).—Palmitic acid (I) (e.g.) of known isotope content is added to the mixture to be analysed, and a small sample of the pure acid is isolated from the mixture. The (I) content of the mixture is calc. from the isotope concn. in the added and extracted samples. The method is also applied to glycine, glutamic acid, and aspartic acid in fibrin hydrolysates. R. L. E.

Determination of lactic and pyruvic acid with periodic acid. R. BOISSON (J. Pharm. Chim., 1940, [ix], 1, 240—255; cf. A., 1940, II, 34).—Air is aspirated through boiling 0.1—1% lactic acid (I) (10 c.c.) containing 10% HIO_4 (10 c.c.) and 10N- H_2SO_4 (2 c.c.) and the MeCHO formed is absorbed in Nessler's reagent and determined titrimetrically (error $\pm 3\%$). 0.5—1 mg. is determined by a modified method. If glucose is mixed with (I), the latter is determined after extraction with ether. AcCO_2H (II) interferes with the determination of (I) unless approx. equimol. amounts of the two substances are present. When (II) (5—30 mg.) is heated (boiling H_2O -bath/0.5—1 hr.) with 0.1N- NaIO_4 (5 c.c.), the excess of NaIO_4 determined titrimetrically is a measure of (II) present. J. L. D.

Polarographic analysis of mixtures of aldehydes and peroxides. V. SCHTERN and S. POLLJAK (J. Gen. Chem. Russ., 1940, 10, 21—30).—The

negative reduction potentials of certain peroxides and aldehydes in 0.1N-LiCl are: MeO_2H and EtO_2H 0.25—0.3, $(\text{OH}\cdot\text{CH}_2)_2\text{O}_2$ 0.35, Et_2O_2 0.5, H_2O_2 0.75, CH_2O 1.55—1.6, MeCHO and EtCHO 1.75—1.8. The polarographic determination of these substances and of their mixtures is described. R. T.

Identification of β -aminoethanol. B. KEISER (Ind. Eng. Chem. [Anal.], 1940, 12, 284).— $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ (I) in H_2O is treated with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, evaporated to dryness, and heated at $210^\circ/5$ min.; $o\text{-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot[\text{CH}_2]_2\cdot\text{OH}$, m.p. 127° , is formed. Similarly, (I) with $\text{H}_2\text{C}_2\text{O}_4$ in H_2O yields the oxalate, m.p. $199\text{--}200^\circ$, which when heated to 220° gives NN' -bis-(β -hydroxyethyl)oxamide, m.p. 168° . J. D. R.

Biuret reaction. B. M. KOSOLAPOV (J. Appl. Chem. Russ., 1940, 13, 314—316).—The biuret reaction is given by salts of Cu^I , Cu^{II} , and Ni^{II} . The violet complex obtained with Co^{II} is readily oxidised by atm. O_2 to a brownish-yellow Co^{III} complex. R. T.

Micro-determination of homocystine.—See A., 1940, III, 550.

Determination of creatinine with m -dinitrobenzoic acid.—See A., 1940, III, 619.

Determination of cholesterol.—See A., 1940, III, 620.

Determination of indole. Modification of Ehrlich's reaction. L. H. CHERNOFF (Ind. Eng. Chem. [Anal.], 1940, 12, 273—274).—Indole in EtOH -free CHCl_3 is treated with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in 85% HPO_3 , and AcOH added; the colour in the HPO_3 layer is compared with known standards. J. D. R.

Volumetric determination of acridines by methylene-blue. A. BOLLIGER (Quart. J. Pharm., 1940, 13, 1—6).—Acridines are determined by pptn. from neutral or slightly acid solution with excess of picric acid (I); after removal of the picrate the excess of (I) is determined by titration with methylene-blue (A., 1939, II, 398). The determination of 2:8-diaminoacridine (*monopicrate*, decomp. 250°), 2:8-diamino-10-methylacridinium chloride [*monopicrate*, m.p. 244° (decomp.)], and their commercial forms proflavine, euflavine, and acriflavine is described. J. N. A.

Precipitating agents for alkaloids and amines. C. C. FULTON (Amer. J. Pharm., 1940, 112, 51—64, 134—154; cf. A., 1932, 629).—A large no. of reagents are described which give characteristic cryst. ppts. with alkaloids. Pptn. is most satisfactory when the alkaloid is dissolved in 85% H_3PO_4 . J. L. D.

Determination of nicotine and anabasine present together. A. SCHMUK and A. BOROZDINA (J. Appl. Chem. Russ., 1939, 12, 1582—1585).—Total alkaloids are determined in a sample of tobacco by titration of the Et_2O extractives. A second portion of the aq. solution of extractives is made acid with H_2SO_4 , filtered, and 3 ml. of 10% H_2SO_4 and 10 ml. of 5% NaNO_2 are added to 50 ml. of filtrate + washings. Nicotine is then pptd. as picrate (nitroso-anabasine is not pptd. under these conditions), and the ppt. is titrated in the usual way. Anabasine is given by difference. R. T.

A., II.—Organic Chemistry

AUGUST, 1940.

Absorption spectra as an aid to research in organic and biological chemistry. A. E. GILLAM (J. Roy. Coll. Sci., 1940, 10, 21—34).—A lecture.

L. J. J.

Catalytic cyclisation of $\beta\zeta$ -dimethyloctane in the presence of platinised charcoal. B. A. KAZANSKI, A. F. PLATE, and E. E. GOLDMAN (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 250—251).—Passage of $\beta\zeta$ -dimethyloctane (I) over platinised charcoal at $\sim 310^\circ$ gave a condensate with increased n indicating the formation of an aromatic hydrocarbon (II). Since (II) is convertible into *p*-cymene- α -sulphonic acid (identified as Ba salt) it is concluded that (I) is partly hydrogenated to *p*-cymene.

W. R. A.

Destructive hydrogenation of high mol. wt. polymerides. *iso*Butene polymeride, butadiene polymeride, and natural rubber. V. N. IPATIEV and R. E. SCHAAD (Ind. Eng. Chem., 1940, 32, 762—764).—Destructive hydrogenation of rubber-like *iso*-butene polymeride (prep. by treating *isobutene* in liquid C_3H_8 with $AlCl_3$ and HCl) at $250^\circ/100$ kg. per sq. cm. initial H_2 pressure, using NiO as catalyst, yields only paraffinic hydrocarbons, indicating that the polymerides probably have long aliphatic C chains. Similar treatment of polymerised butadiene (prep. by heating butadiene at $150^\circ/40$ atm. and freeing the product from oils of b.p. $<300^\circ$ by vac. distillation) and of rubber yields only naphthenic hydrocarbons, principally ethylcyclohexane and *p*-menthane, respectively. Hydrogenation of *isoprene* at $250^\circ/100$ atm. H_2 in presence of NiO yields $EtPr^s$ (32 wt.-%) and a polymeric compound, b.p. 155 — 190° .

J. W. S.

Action of fluorine vapour on organic compounds. VIII. Influence of dilution on vapour-phase fluorination of ethane. DEW, S. YOUNG, N. FUKUHARA, and L. A. BIGELOW (J. Amer. Chem. Soc., 1940, 62, 1171—1173; cf. A., 1940, II, 147).—In presence of Cu gauze, C_2H_6 and F_2-N_2 give $(CHF_2)_2$, $CHF_2\cdot CH_2F$, and *pentafluoroethane*, f.p. -103° , b.p. $-38^\circ/1200$ mm., $-48.5^\circ/760$ mm., the proportions varying according to those of the reactants.

R. S. C.

Catalytic hydration of olefines. III. Sulphuric acid as a catalyst for continuous preparation of *tert*-butyl alcohol from *isobutylene*. E. K. REMIZ and A. V. FROST (J. Appl. Chem. Russ., 1940, 13, 210—214; cf. A., 1936, 819).— $CH_3\cdot CMe_2$ is passed through 3% Ag_2SO_4 in 10% H_2SO_4 at 90 — 95° , the issuing gas is passed through a condenser and then back to the process, and Bu^oOH condensing is

collected. H_2O is added continuously to the reaction vessel, to maintain const. $[H_2SO_4]$. R. T.

Synthesis of choline β -glycerophosphate. H. ARNOLD (Ber., 1940, 73, [B], 87—90; cf. Contardi *et al.*, A., 1933, 863).— $Na_2\beta$ -glycerophosphate with $AcOH$ (to neutrality) and $AgNO_3$ gives $Ag_2\beta$ -glycerophosphate (I), which with $Br[CH_2]_2\cdot NMe_3Br$ in boiling $EtOH$ under N_2 yields *choline* β -glycerophosphate (II), b.p. 104 — 105° , strongly hygroscopic, decomposed by $CdCl_2$. With $Br[CH_2]_2\cdot NH_2\cdot HBr$, (I) gives a resinous product, *colamine* α -glycerophosphate (?) (cf. Feulgen *et al.*, A., 1939, III, 915), m.p. 80 — 90° (sinters 60°). (II) has 0.001 of the activity of acetylcholine (III) on the frog's heart and on blood pressure in the cat. Its activity on intestinal and skeletal muscle is similar to but much weaker than that of (III). Its activity at 10^{-5} on the leech is equiv. to that of (III) at 10^{-8} . When heated at 100° , (II) is first activated (due to hydration?) and then deactivated. E. W. W.

Preparation of branched-chain aliphatic sulphonic acids. S. ZUFFANTI (J. Amer. Chem. Soc., 1940, 62, 1044).— RBr and boiling, aq. Na_2SO_4 give 56.8—95.7% of RSO_3Na and thence by $HCl-Et_2O$ *propane*- β -, m.p. -37° (109°), β -methyl-*n*-*propane*- α -, m.p. -61° (123°), γ -methyl-*n*-*butane*- α -, m.p. -5° (115°), and *isobutane*- β -, m.p. -76° (131°), -sulphonic acid, figures in parentheses being m.p. of the $m-C_6H_4MeNH_2$ salts. R. S. C.

Reaction of sulphur with mercuric acetate in glacial acetic acid. R. E. VALLRATH (J. Amer. Chem. Soc., 1940, 62, 1310).—At 135° the reaction, $6Hg(OAc)_2 + S \rightarrow 6HgOAc + 6AcOH + H_2SO_4$, occurs in $AcOH$. Prolonged heating gives a little org. Hg compound. R. S. C.

Mechanism of esterification of strong organic acids. I. Esterification of neopentyl alcohol with the chloroacetic acids. O. R. QUAYLE and H. M. NORRIS (J. Amer. Chem. Soc., 1940, 62, 1170—1171).— CH_2Bu^oOH (I) (prep. from $MgBu^oCl$ and gaseous CH_2O) gives neopentyl acetate, b.p. 127° , *chloro*-, b.p. 180° , *dichloro*-, b.p. 194° , and *trichloro*-acetate, b.p. 202° , *p*-nitro-, m.p. 54 — 54.5° , and 3:5-dinitro-benzoate, m.p. 90 — 90.5° . Absence of unsaturation (Br) and hydrolysis to (I) prove that during esterification isomerisation does not occur and thus that the C-O linking remains intact. R. S. C.

Addition of hydrogen bromide to methyl methylacrylate. C. C. PRICE and E. C. COYNER (J. Amer. Chem. Soc., 1940, 62, 1306—1307).— $CH_2\cdot CMe\cdot CO_2Me$ and HBr give under all conditions $CH_2Br\cdot CHMe\cdot CO_2Me$. $CMe_2Br\cdot CO_2Me$ is prepared

for comparison from $\text{Pr}^s\text{CO}_2\text{H}$ by red P-Br etc. Physical consts. are recorded. R. S. C.

Carbonation of organoalkali compounds. H. GILMAN and H. A. PACEVITZ (J. Amer. Chem. Soc., 1940, 62, 1301—1302).—Interaction of $n\text{-C}_5\text{H}_{11}\text{Cl}$ and Na in light petroleum and spraying the products on to solid CO_2 gives 36.4—51.5% of $n\text{-C}_5\text{H}_{11}\text{CO}_2\text{H}$ (I) and <2% of $\text{CHBu}^n(\text{CO}_2\text{H})_2$ (II). Gaseous CO_2 gives 15.2—19.5% of (I) and 14.8—31.4% of (II). R. S. C.

Fatty acids. VI. Crystallisation methods in the isolation of arachidonic acid; comparison of the properties of this acid prepared by crystallisation and by debromination. Structure of arachidonic acid. G. Y. SHINOWARA and J. B. BROWN (J. Biol. Chem., 1940, 134, 331—340).—Crystallisation from COMe_2 of the esters of adrenal phosphatides yields 70—75% pure Me arachidonate, distillation of which yields the 95% pure ester (I). The properties of (I) are compared with those of the ester obtained by the bromination-debromination method. Comparison of the octabromide of (I), and of the arachidic acid obtained by reduction and its Me and Et esters, with synthetic specimens confirms their straight-chain structure. Ozonisation and oxidation ($\text{KMnO}_4\text{-COMe}_2$) of (I) yields MeCHO , succinic and adipic acids, but not malonic, oxalic, or azelaic acid. The $\Delta^{8,9}$ structure is suggested. A. Li.

Hydrolysis of fats and fatty acid esters. VIII. T. Ono (J. Agric. Chem. Soc. Japan, 1940, 16, 439—453; cf. A., 1940, I, 260).—Selective hydrolysis of mixed glycerides is more readily carried out in heterogeneous than in homogeneous systems. More highly unsaturated acid radicals are more readily split off from fish oils by lipase or KOH at -10° than less saturated or saturated radicals. H. G. R.

Separation of hydroxy- from non-hydroxy-aliphatic acids by means of a dibasic acid anhydride. F. E. KURTZ and P. S. SCHAFFER (J. Amer. Chem. Soc., 1940, 62, 1304—1305).—The mixed saturated esters are heated with $(\text{CH}\cdot\text{CO})_2\text{O}$ (I) at 120° , and the product is dissolved in light petroleum and extracted with dil. KOH. For unsaturated esters $(\text{CH}_2\cdot\text{CO})_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$ at 130° (some tar formed) is preferable, as a side-reaction occurs with (I). R. S. C.

Increase in optical rotation of *d*-lactic acid. S. FUKUDA (J. Biochem. Japan, 1939, 30, 473—477).—With 23.4% aq. *d*-lactic acid (I), addition of H_3BO_3 up to a concn. of 2.5% increases $[\alpha]^{18}$ progressively from $+2.14^\circ$ to $+5.12^\circ$; borax gives a max. increase at a concn. of 2.0%, higher concns. (up to 3.35%) decreasing $[\alpha]$. $\text{UO}_2(\text{NO}_3)_2$, especially in presence of KOH, and $\text{NHPh}\cdot\text{NH}_2$ increase $[\alpha]$, whilst $(\text{NH}_4)_2\text{MoO}_4$ gives a 50-fold increase [max. at 1 mol. per 5 mols. of (I)]. F. O. H.

Phosphorylated oxidation product of pyruvic acid. F. LIPMANN (J. Biol. Chem., 1940, 134, 463—464; cf. A., 1939, III, 1100).— AcCO_2H is oxidised by enzyme solutions from *B. delbrückii* in presence of inorg. PO_4''' (with or without F'). The quantity of the latter (determined by deproteinisation with $\text{CCl}_3\text{CO}_2\text{H}$, neutralisation, and pptn. with

CaCl_2) decreases by an amount nearly equiv. to the extra O used, an unstable org. phosphate being formed which behaves like acetyl phosphate. A. Li.

Synthesis of serine. J. L. WOOD and V. DU VIGNEAUD (J. Biol. Chem., 1940, 134, 413—416).—Equimol. quantities of $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ and NaOEt at 0° give an 80—85% yield of $\text{OEt}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ (NaOMe gives poorer yields of the OMe-compound), for the synthesis of serine (A., 1937, II, 53). A. Li.

Extension of Reformatsky reaction. I. Ethyl bromomalonate and acetone. B. H. IYER (J. Indian Chem. Soc., 1940, 17, 215—218).— $\text{CHBr}(\text{CO}_2\text{Et})_2$ with Zn and excess of COMe_2 yields $\text{CH}_2\text{Ac}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ (I), also obtained from $\text{CMe}_2\cdot\text{CH}\cdot\text{COMe}$ (II) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (Quadrat-i-Khuda, A., 1929, 295), or by using (II) or diacetone alcohol instead of COMe_2 . With only 1 mol. of COMe_2 , (I) is obtained together with some (II) and unchanged reactants. The mechanism of the formation of (I) is discussed. A. Li.

Addition of $\alpha\beta$ -unsaturated alcohols to the active methylene group. I. Action of ethyl acetoacetate on linalool and geraniol. M. F. CARROLL (J.C.S., 1940, 704—706).—With $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (I) at $140\text{--}210^\circ$, linalool gives geranylacetone (II) (cf. Foster *et al.*, J.C.S., 1913, 103, 1345) (55% yield), with an isomeric ketone, and the acetate, b.p. $84\text{--}86^\circ/1\text{ mm.}$, of an alcohol, b.p. $82\text{--}85^\circ/1.5\text{ mm.}$ With (I) at 200° , geraniol gives geranyl acetate, and (II) (19% yield). E. W. W.

Polyhydric alcohol-polybasic acid reaction. V. Glycerol succinate and maleate polyesters. R. H. KIENLE and F. E. PETKE (J. Amer. Chem. Soc., 1940, 62, 1053—1056; cf. A., 1939, II, 506).—Interaction of glycerol with $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ and with $(\text{CH}_2\cdot\text{CO})_2\text{O}$ is similar after 50% esterification. < the theoretical amount of H_2O is evolved, probably owing to retention of H_2O by the product. Interaction with $(\text{CH}\cdot\text{CO})_2\text{O}$ leads to liberation of > the theoretical amount of H_2O , owing to anhydride formation and intra-esterification. Gelation of the products is associated with low mol. wt. (1100—1200). R. S. C.

Action of sodium alkoxides on ethyl *s*-diethoxy-succinate. II. Mechanism of formation of ethyl *as*-diethoxysuccinate from ethyl disodio-tricartrate. S. FUKUNAGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1940, 37, 216—220; cf. A., 1940, II, 243).—Isomerisation of $d\text{-}[\text{CH}(\text{OEt})\cdot\text{CO}_2\text{Et}]_2$ to $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})_2\cdot\text{CO}_2\text{Et}$ (I) is easily effected by NaOEt , less easily by $[\text{CH}(\text{ONa})\cdot\text{CO}_2\text{Et}]_2$ (II), and scarcely by $\text{CO}_2\text{Et}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{ONa})\cdot\text{CO}_2\text{Et}$. The change follows the course, (II) $\rightarrow [\text{CH}(\text{OEt})\cdot\text{CO}_2\text{Et}]_2 \rightarrow \text{trans-CO}_2\text{Et}\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CO}_2\text{Et} \rightarrow$ (I). H. W.

Fully acetylated sugar acids and their derivatives. G. B. ROBBINS and F. W. UPSON (J. Amer. Chem. Soc., 1940, 62, 1074—1076).—Glucose and O_2 in 2N-KOH give K *d*-arabonate, which by way of the Ca and Na salt yields *d*-arabonic acid, m.p. $114\text{--}116^\circ$, $[\alpha] +10.5^\circ$ in H_2O , or by way of the Ca salt and lactone *d*-arabonamide, m.p. $138\text{--}139^\circ$, $[\alpha] +38.6^\circ$ in H_2O . The appropriate amide with ZnCl_2 in Ac_2O

at 0° gives *d-arabonamide tetra-acetate*, m.p. 123°, $[\alpha] +24.3^\circ$, *d-talonamide penta-acetate*, m.p. 104—106°, $[\alpha] +85.4^\circ$, and *d-galaheptonamide hexa-acetate*, m.p. 185—187°, $[\alpha] +2.1^\circ$. The crude or pure amide with N_2O_3 (A., 1938, II, 124) gives *d-arabonic acid tetra-* (I), m.p. 135—136°, $[\alpha] +32.5^\circ$ (phenylhydrazide, m.p. 140—141°, $[\alpha] +8.4^\circ$; *Me* ester, m.p. 136°, $[\alpha] +42.3^\circ$), *d-mannonic acid penta-* (II), $+H_2O$, m.p. 75—76°, $[\alpha] +24.8^\circ$ (phenylhydrazide, m.p. 173°, $[\alpha] +13.0^\circ$), *d-talonic acid penta-* (III), m.p. 142—144°, $[\alpha] +78.3^\circ$ (phenylhydrazide, m.p. 162—163°, $[\alpha] +35.0^\circ$; *Me* ester, m.p. 78—79°, $[\alpha] +70.1^\circ$), *d-gulonic acid penta-* (IV), a syrup, $[\alpha] +1.8^\circ$ (phenylhydrazide, a syrup, $[\alpha] +37.7^\circ$; *Me* ester, a syrup, $[\alpha] +4.4^\circ$), and *d- α -glucoheptonic acid hexa-* (V), $+0.5H_2O$, m.p. 94°, $[\alpha] +10.7^\circ$ (phenylhydrazide, m.p. 154°, $[\alpha] +27.4^\circ$; *Me* ester, m.p. 93°, $[\alpha] +14.1^\circ$), *-acetate*. Direct acetylation of the acid yields (I), (III), *d-galactonic acid penta-acetate* (phenylhydrazide, m.p. 220°, $[\alpha] +23.6^\circ$; *Me* ester, m.p. 126—127°, $[\alpha] +2.5^\circ$), and *d- α -galaheptonic acid hexa-acetate*, m.p. 176—177°, $[\alpha] +15.3^\circ$ (phenylhydrazide, m.p. 112—114°, $[\alpha] +25.0^\circ$; *Me* ester, m.p. 96—97°, $[\alpha] +18.8^\circ$). *d-Arabanolactone triacetate*, m.p. 68—69°, $[\alpha] +52.3^\circ$, and *d- α -galaheptonolactone penta-acetate*, m.p. 123—124°, $[\alpha] -16.9^\circ$, are prepared from the lactone by Ac_2O at 0°. Attempts to prepare (II), (IV), and (V) from the Na salts of the OH-acids by Ac_2O - $AcOH$ give the acetylated lactones. *Me d-gluconate penta-acetate* has m.p. 124°, $[\alpha] +9.2^\circ$. Phenylhydrazides named above are prepared from the unacetylated phenylhydrazides by Ac_2O - $ZnCl_2$ at 0°. *Me* esters are prepared from the acetylated acids by CH_2N_2 . Unless otherwise stated, $[\alpha]$ are $[\alpha]_D^{25}$ in $CHCl_3$.

R. S. C.

Mutarotation and rotatory dispersion of derivatives of aldehydo-d-galacturonic acid. R. J. DIMLER and K. P. LINK (J. Amer. Chem. Soc., 1940, 62, 1216—1219).—The tetra-acetate of *Me d-galacturonate Et mercaptal* (modified prep.) gives (method: A., 1930, 1021) *Me aldehydo-d-galacturonate tetra-acetate* (I), m.p. 135—136°, $[\alpha]_{589}^{25} -15.6^\circ$ in $CHCl_3$, which yields, according to the method used, the α -, macro-m.p. 105—107°, micro-m.p. 135—136° after loss of $EtOH$ at $\sim 105^\circ$, $[\alpha]_{589}^{25} +40.7^\circ \rightarrow +7.1^\circ$ (no min.) in $CHCl_3$, or β -*Et semiacetal*, macro-m.p. 127—130°, micro-m.p. 135—136° after loss of $EtOH$ at $\sim 127^\circ$, $[\alpha]_{589}^{25} -6.7^\circ \rightarrow +7.1^\circ$ (min. -10.0°) in $CHCl_3$, the min. in $[\alpha]$ being due to rapid formation of (I) as intermediate in the mutarotation. *Et d-galacturonate Et mercaptal*, m.p. 128—129°, $[\alpha]_{589}^{25} +15.7^\circ$ in $EtOH$ (tetra-acetate, m.p. 80—81°, $[\alpha]_{589}^{25} +11.0^\circ$ in $CHCl_3$), *Et aldehydo-d-galacturonate tetra-acetate* (II), m.p. 95—97°, $[\alpha]_{589}^{25} -24.0^\circ$ in $CHCl_3$, and *Et d-galacturonate tetra-acetate β -Et semiacetal*, m.p. 105—106°, $[\alpha]_{589}^{25} -14.4^\circ \rightarrow -1.6^\circ$ (no min.) in $CHCl_3$, are also prepared. The rotatory dispersion of (I) and (II) agrees with two-term Drude equations.

R. S. C.

Esters of alginic acid. H. J. LUCAS and W. T. STEWART (J. Amer. Chem. Soc., 1940, 62, 1070—1074).— HNO_3 - H_2SO_4 introduces into alginic acid 0.49—1.2 NO_2 per mannuronic acid unit. The product lactonises when dried, but can be partly methylated without replacement of NO_2 . Methyl-

ation of (I) is slow (CH_2N_2 ; affects CO_2H and OH) or accompanied by degradation (Me_2SO_4). R. S. C.

Rates of formation of sulphoaliphatic acids.—See A., 1940, I, 326.

Aldehyde complexes of copper salts. T. L. DAVIS and W. P. GREEN, jun. (J. Amer. Chem. Soc., 1940, 62, 1272—1274).—Prep. and dissociation pressure of compounds, $CuNCS.MeCHO$, $2CuI.MeCHO$, $Cu(OAc)_2.MeCHO$, $2CuNCS.PrCHO$, and $3CuI.PrCHO$, and the v.p. of $PrCHO$ are recorded. R. S. C.

Chlorination and structure of acetylketen. C. D. HURD and J. L. ABERNETHY (J. Amer. Chem. Soc., 1940, 62, 1147—1148).—Keten dimeride (I) and Cl_2 in CCl_4 give γ -chloroacetoacetyl chloride (II), b.p. 93—96° (decomp.)/8 mm. (cf. Boese, A., 1940, II, 65), which with NH_2Ph in C_6H_6 gives γ -chloroacetoacetyl anilide, m.p. 140—141°. Crude (II) and $EtOH$ at 0° give $CH_2Cl.CO.CH_2.CO_2Et$, b.p. 117—119°/17 mm. (I) is probably a mixture of $COMe.CH.CO$ and crotono- β -lactone. R. S. C.

Keten acetals. V. Reaction of keten diethyl acetal with compounds containing an active hydrogen [atom]. H. M. BARNES, D. KUNDIGER, and S. M. McELVAIN (J. Amer. Chem. Soc., 1940, 62, 1281—1287; cf. A., 1940, II, 202).—Most compounds containing active H attached to halogen, O, C, or N add to $CH_2:C(OEt)_2$ (I) by attachment of the H to CH_2 , but $CH_2Ac.CO_2Et$ and $CH_2(CO_2Et)_2$ add as H and $CHAc.CO_2Et$ and $CH(CO_2Et)_2$, respectively. The latter additions are catalysed by $NaOEt$, the function of which is discussed. HBr and (I) in Bu_2O give $EtBr$ (85%) and $EtOAc$ (72%) by way of $CMeBr(OEt)_2$. 3:5:1- $(NO_2)_2C_6H_3.CO_2H$ and (I) in Et_2O give 3:5:1- $(NO_2)_2C_6H_3.CO_2Et$ (74%). $PhOH$ and (I) give $PhOEt$ (78%), $EtOAc$ (59%), and $PhOAc$ (17%). CH_2Bz_2 and (I) give *Ph β - α' -diethoxyethoxy- β -phenylvinyl ketone*, $CMe(OEt)_2.O.CPh.CH.COPh$, m.p. 86—87°, hydrolysed by 5% H_2SO_4 to $EtOH$, $AcOH$, and CH_2Bz_2 , and pyrolysed at $140^\circ/38$ mm. in N_2 to (I) (31%) and CH_2Bz_2 (61%). $CH_2Ac.CO_2Et$ (1 mol.), (I) (2 mols.), and $NaOEt$ (0.01 mol.) at 85° give $CMe(OEt)_3$ (78%) and much *Et α - α' -ethoxyethylidenacetate*, b.p. 96—98°/1 mm. [hydrolysed by H_2O (2 mols.) in dioxan to $AcOH$ (92%) or by H_2O (1 mol.) in dioxan to $CHAc.CO_2Et$], with some $EtOH$ and $EtOAc$. $CH_2(CO_2Et)_2$, (I), and a little $NaOEt$ at 125° give *Et α -ethoxyethylidenemalonate* (55%), m.p. 26—27° (lit. an oil), b.p. 100—102°/1 mm., hydrolysed by hot 2*N*- HCl to $CHAc.CO_2Et_2$ and hydrogenated (Raney Ni; $EtOH$; $100^\circ/2800$ lb.) to *Et α -ethoxyethylmalonate*, b.p. 66—67°/0.4 mm. $CHMe(CO_2Et)_2$ does not react with (I). $CH_2(SO_2Ph)_2$ and (I) in dioxan give tars. NH_3 and (I) at 110° give $EtOH$, $MeCN$, $NH.CMe.NH_2$, and $CMe(OEt)_3$ ($OEt.CHMe.NH$ is an intermediate). NH_2Ph and (I) give $EtOH$ (86%), $NPh.CH.CO_2Et$, and a little $NPh.CMe.NHPh$. $NHPhEt$ and (I) at 100° give $CMe(OEt)_3$ and *N-ethyl-N- α -ethoxyvinylaniline*, b.p. 129—130°/22 mm., hydrolysed to $NHPhEt$, $EtOH$, and $AcOH$. Boiling piperidine and (I) give 43% each of $CMe(OEt)_3$ and $\alpha\alpha$ -tripiperidinoethane, b.p. 113—115°/1 mm., hydro-

lysed by boiling 6N-H₂SO₄ to piperidine (83%) and AcOH (110%). R. S. C.

Crystalline phenylurethanes of sugar glucosides. M. L. WOLFFROM and D. E. FLETCHER (J. Amer. Chem. Soc., 1940, 62, 1151—1153).—The appropriate methylglucoside and PhNCO in boiling, dry C₅H₅N give α -, m.p. 227° (decomp.), $[\alpha]_D^{25} +73^\circ$ in COMe₂, and β -methyl-d-glucoside tetra-, m.p. 225° (decomp.), $[\alpha]_D^{25} +13^\circ$ in C₅H₅N, β -methyl-d-xyloside tri-, m.p. 234° (decomp.), $[\alpha]_D^{25} -23^\circ$ in COMe₂, and α -methyl-d-mannoside tetra-, m.p. 189—190° (decomp.), $[\alpha]_D^{25} -18^\circ$ in COMe₂, -phenylurethane. R. S. C.

Action of phosphorus pentachloride on aldehyde-galactose penta-acetate. 1:1-Dichloride of aldehyde-galactose penta-acetate. M. L. WOLFFROM and D. I. WEISBLAT (J. Amer. Chem. Soc., 1940, 62, 1149—1151).—aldehyde-d-Galactose penta-acetate (I) and PCl₅ in boiling Et₂O give di-(1-chloro-aldehyde-d-galactose penta-acetate) chlorophosphate, (OAc·CH₂·[CH(OAc)]₄·CHCl·O)₂·POCl (II), m.p. 190° (decomp.), $[\alpha]_D^{25} -20^\circ$ in CHCl₃, and a trace of 1:1-dichloro-aldehyde-d-galactose penta-acetate, OAc·CH₂·[CH(OAc)]₄·CHCl₂ (III), m.p. 148—150°, $[\alpha]_D^{25} +11^\circ$ in CHCl₃ (better obtained in boiling C₆H₆—CaSO₄ under defined conditions), which both reduce Fehling's solution only slowly. Hydrolysis of (II) by Ag₂O and a little H₂O in boiling PhMe gives (I). With boiling HCl—EtOH or —MeOH, (II) gives Et (IV), m.p. 156—158°, $[\alpha]_D^{25} -24^\circ$ in CHCl₃, and Me di-(1-chloro-aldehyde-d-galactose penta-acetate) phosphate, (OAc·CH₂·[CH(OAc)]₄·CHCl·O)₂·PO₂R, m.p. 187—188° (decomp.), $[\alpha]_D^{25} -19^\circ$ in CHCl₃, respectively. With ZnCl₂—Ac₂O at 98°, (IV) gives aldehyde-d-galactose hepta-acetate (V). Boiling, aq. Cu(OAc)₂ is reduced by d-galactose, (I), aldehyde-d-galactose Pr^F semiacetal, (V), 1-chloro-d-galactose hexa-acetate, 1-methoxy-d-galactose hexa-acetate, 1-chloro-1-ethoxy-d-galactose penta-acetate, and d-galactopyranose tetra-acetate, but not by β - or α -d-galactopyranose penta-acetate, (II), or (III); the test has diagnostic val. R. S. C.

aldehyde-Maltose octa-acetate. M. L. WOLFFROM and M. KONIGSBERG (J. Amer. Chem. Soc., 1940, 62, 1153—1154).—Maltose Et₂ mercaptal octa-acetate, HgCl₂, CdCO₃, and H₂O in COMe₂ give 78% of aldehyde-maltose octa-acetate, m.p. 116—117°, $[\alpha]_D^{25} +93.5^\circ$ in CHCl₃, $[\alpha]_D^{25} +96^\circ$ in EtOH, and (+EtOH) m.p. 66—67° (oxime, m.p. 93—94°, $[\alpha]_D^{25} +107^\circ$ in CHCl₃, +100° in EtOH) (cf. A., 1939, II, 202). R. S. C.

Constitution of amylose and amylopectin of maize starch. K. H. MEYER (Arch. Sci. phys. nat., 1940, [v], 22, Suppl., 19—23).—Extraction of maize starch with H₂O at 70° and cooling gives cryst. amylose (I). Fractionation of this yields an insol. variety which gives no reaction with I, and reverts to a sol. form when dissolved in aq. chloral and pptd. with COMe₂. The Ac derivative in CHCl₃ has η little < that of cellulose acetate; measurements of its osmotic pressure show that the amylose has mol. wt. 20,000—50,000. The Ac₃ and Me₃ derivatives give films resembling those of cellulose. Amylopectin has mol. wt. 400,000, and gives clear solutions (without scission) in aq. chloral at 80° or in aq. N₂H₄ or

(CH₂·NH₂)₂ at room temp. Pptn. of the aq. chloral solution with COMe₂ yields a temporarily sol. form which turns blue with I. The Me₃ and Ac derivatives give brittle films; η of the latter in CHCl₃ is <20%, and that of its acid hydrolysis products 25%, of the vals. for cellulose derivatives. (I) is hydrolysed completely by β -amylase to maltose, but (II) only partly, to a dextrin of mol. wt. 150,000. It is concluded that (I) has straight, and (II) branched, mols. A. LI.

Structure of the dextran synthesised from sucrose by *Betacoccus arabinosaceus*, Orla-Jensen. W. Z. HASSID and H. A. BARKER (J. Biol. Chem., 1940, 134, 163—170).—Sucrose with *B. arabinosaceus* yields a non-reducing dextran (I), $[\alpha]_D +184^\circ$ in N-NaOH, mol. wt. 11,700 (Staudinger) or 2600 (sedimentation equilibrium method). Hydrolysis (dil. HCl) of (I) gives glucose, the downward mutarotation indicating that the units of (I) have the α configuration. Acetylation (AcOH containing Cl₂, then Ac₂O containing SO₂) of (I) followed by hydrolysis yields a H₂O-sol. form, $[\alpha]_D +180^\circ$ in H₂O. Methylation (Me₂SO₄, followed by Na, MeI, and liquid NH₃ in PhOMe) of (I) yields a product, $[\alpha]_D +214^\circ$ in CHCl₃, hydrolysed (aq. AcOH—HCl) to 2:3:4-trimethyl- and 2:3:4:6-tetramethyl-glucose in the mol. ratio 15:1. A. LI.

Degradation of long-chain molecules. H. MARK and R. SIMHA (Trans. Faraday Soc., 1940, 36, 611—618).—Cellulose acetate (Ac 39.3%, mol. wt. ~93,000) was subjected to homogeneous acetolysis (Ac₂O + AcOH), and distribution curves for the degradation products were obtained at four different stages of the reaction. The results are in qual. agreement with the theory of Kuhn (A., 1932, 576) and Flory (A., 1936, 1452). F. L. U.

Similarity of cellulose to caoutchouc and the production of artificial cellulose threads as a macromolecular process. P. H. HERMANS (Naturwiss., 1940, 28, 223).—The very pronounced similarity of caoutchouc to cellulose shows that the latter does not occupy a unique position as a micellary substance under all conditions but must be regarded in the same manner as the other complex polymerides. Macromol. processes are mainly operative in the production of artificial fibres and in deformation processes.

H. W.

Unusual hydrates of quaternary ammonium salts. D. L. FOWLER, W. V. LOEBENSTEIN, D. B. PALL, and C. A. KRAUS (J. Amer. Chem. Soc., 1940, 62, 1140—1142).—The prep. and analysis of the following compounds are given (m.p. in parentheses): NBu⁺₄·OH, xH₂O [$x = 31$ (30.2°), 4 (26°), 2]; NBu⁺₄·F, 18H₂O (37°); N(iso-C₅H₁₁)₄·OH, xH₂O [$x = 32$ (31°), 4 (57.5°)]; N(n-C₅H₁₁)₄·OH, 4H₂O; (Bu⁺₄N)₂C₂O₄·38H₂O (20—25°); HCO₂NBu⁺₄·33H₂O (12.5°); NBu⁺₄·Br, 26H₂O (14.5°); HCO₂N(iso-C₅H₁₁)₄·50H₂O (15—20°); NBu⁺₄·OAc, 60H₂O (10—15°); EtCO₂NBu⁺₄·50H₂O (17°); NBu⁺₄·OBz, 35H₂O (3.5°); NBu⁺₄·NO₃, 27H₂O (5.8°); NBu⁺₄·Cl, 30H₂O (15°). Several salts which do not yield hydrates are listed. NMe₄·OH, 5H₂O was prepared and NPr⁺₄·OH, and NEtPr⁺₃·OH were obtained. W. R. A.

Reaction of the esters of *dl*-leucine and *l*-leucine on Raney catalyst. G. OVAKIMIAN, C. C. CHRISTMAN, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1940, 134, 151—161).—Hydrogenation (H_2 under pressure, Raney Ni) of *dl*-leucine Et ester in MeOH yields, at 135°, *dl*-leucinol, and at 185° or 200°, *NN*-dimethyl-leucinol, $CHMeBu^{\beta}NMe_2$ (I), and 2:5- and *NN'*-dimethyl-2:5-diisobutylpiperazine (II), in proportions varying according to time and temp. *l*-Leucine Et ester with excess of catalyst at 70° gives *l*-leucinol, b.p. 130°/18 mm., $[\alpha]_D^{25} +3.8^\circ$ in MeOH (*picrate*, m.p. 120—121°, $[\alpha]_D^{25} +5.9^\circ$ in MeOH). Hydrogenation of leucinol or *NN*-dimethyl-leucinol at 185° gives only (I). *dl*-Leucine Me ester when heated at 150° in MeOH under pressure, with or without H_2 , gives 3:6-diketo-2:5-di-*n*-propylpiperazine, converted by H_2 -catalyst under pressure at 200° into (II). Glycylglycine anhydride similarly yields *NN'*-dimethylpiperazine. The mechanism of these reactions is discussed. A. LI.

Determination of valine and leucine in presence of other amino-acids. C. FROMAGEOT and P. HEITZ (Enzymologia, 1939, 6, 258—270).—Valine (I) is determined by converting, with HNO_2 , into the corresponding α -OH-acid (Kendall and Friedemann, A., 1931, 246), which is heated at 100° under pressure with CrO_3 in AcOH for 3 hr. $COMe_2$ produced (65% of the theoretical yield) is distilled and colorimetrically determined by a modification of the method of Urbach (*ibid.*, 1082). Leucine (II) is determined in the same way but the period of heating is 4 hr. and the yield of $COMe_2$ is 58%. Other NH_2 -acids, including isoleucine, do not interfere in either case. When (I) and (II) are present together one determination is made as for (II) alone and in a second determination, the conc. solution of OH-acids is oxidised at atm. pressure so that the $COMe_2$ produced is directly distilled. The yields of $COMe_2$ obtained when (I) and (II) are separately determined by the second method are 72 and 21%, respectively. The proportions of the acids are calc. according to a formula given. The amounts of each acid required for the determination are 2—20 mg. W. MCC.

Racemisation of glutamic acid. J. M. JOHNSON (J. Biol. Chem., 1940, 134, 459).—*l*(+)-Glutamic acid hydrochloride undergoes 4.6% racemisation when boiled with conc. HCl for 35 hr. The *d*(-)-acid in protein hydrolysates is presumably formed by similar racemisation. A. LI.

Pantothenic acid diphosphoric acid. D. W. WOOLLEY (J. Biol. Chem., 1940, 134, 461—462; cf. A., 1940, III, 537; II, 203).— $OAc\cdot CH_2\cdot CHMe_2\cdot CH(OAc)\cdot COCl$ with $NH_2\cdot [CH_2]_2\cdot CO_2Et$, followed by selective hydrolysis, yields pantothenic acid (*Ba* salt), which with $POCl_3$ in C_6H_5N gives the diphosphoric acid, which is biologically inactive, though the crude phosphorylated mixture has some activity. A. LI.

Action of 4-amino-2-methyl-1-naphthol on the oxidation of certain thiol groups. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1940, 134, 457—458).—1:2:4- $OH\cdot C_{10}H_7Me\cdot NH_2\cdot HCl$ catalyses the oxidation (not inhibited by cyanide) to disulphide

of cysteine or $SH\cdot CH_2\cdot CO_2H$ at pH 7.8, rapidly oxidises SH groups in rat liver nucleoprotein, and causes a 50% inhibition in the action of cryst. papain hydrochloride on milk, but has little effect on the oxidation of reduced glutathione. The physiological significance of these effects is discussed. A. LI.

α -Bromo- α -sulphonamides. W. M. ZIEGLER and R. CONNOR (J. Amer. Chem. Soc., 1940, 62, 1049—1053).—The products considered by Tröger *et al.* (A., 1905, i, 336) to be $RSO_2\cdot CHR'\cdot CO\cdot NHBr$ are $RSO_2\cdot CR'Br\cdot CO\cdot NH_2$ (A) and contain "positive" Br. α -Bromo-*p*-toluene- (I), m.p. 172—174°, and α -bromo-*n*-butane- α' -sulphonylacetamide, m.p. 130—131°, α -bromo- α -*p*-toluene- (II), m.p. 115—116°, and α -bromo-*n*-butane- α' -sulphonyl-*n*-butylamide (III), m.p. 57—58°, are best obtained by brominating $RSO_2\cdot CHR'\cdot CO\cdot NH_2$, usually in moist CCl_4 ; sometimes the reactions, $RSO_2\cdot CHR'\cdot CO_2H \rightarrow RSO_2\cdot CHR'\cdot COCl \rightarrow RSO_2\cdot CR'Br\cdot COCl \rightarrow$ (A), are feasible, although yields are smaller. NaOBr is less satisfactory, e.g., yields $p\text{-}C_6H_4Me\cdot SO_2\cdot CHBr_2$ in place of (I). Under some conditions (A; R = H) is replaced by $\alpha\alpha$ -dibromo-*p*-toluene-, m.p. 134—135°, and *n*-butane- α' -sulphonylacetamide, m.p. 106—107°. $Bu^{\alpha}SNa$ and (II) in EtOH give $p\text{-}C_6H_4Me\cdot SO_2\cdot CHEt\cdot CO\cdot NH_2$ (60%); $p\text{-}C_6H_4Me\cdot SNa$ and (III) similarly give $(p\text{-}C_6H_4Me\cdot S)_2$ and $Bu^{\alpha}SO_2\cdot CHEt\cdot CO\cdot NH_2$ (IV) (73%). All the Br-amides liberate 2 I from HI and with N_2H_4 give N_2 (Br_2 -amides more rapidly than Br_1 -amides). Piperidine and (I) in dioxan give the hydrobromide (60%) and $p\text{-}C_6H_4Me\cdot SO_2\cdot CH_2\cdot CO\cdot NH_2$ (45%). NaOEt-EtOH with (I) gives $p\text{-}C_6H_4Me\cdot SO_2\cdot CH_2Br$ (also obtained by boiling 5% NaOH) and with (III) gives 61% of (IV). M.p. are corr. R. S. C.

Rate of reaction of Grignard reagent with ethyl bromide.—See A., 1940, I, 326.

Redistribution reaction. V. PbR_4 compounds. G. CALINGAERT, H. A. BEATTY, and H. SOROOS. VI. Lead alkyl halides. G. CALINGAERT, H. SOROOS, and H. SHAPIRO. VII. Alkyl compounds of mercury, tin, silicon, and zinc. G. CALINGAERT, H. SOROOS, and V. HNIZDA (J. Amer. Chem. Soc., 1940, 62, 1099—1104, 1104—1107, 1107—1110; cf. A., 1940, II, 72).—V. The redistribution reaction leads to random distribution of products from $PbMe_4$ - $PbEt_4$, $PbMe_3Et$ - $PbMeEt_3$, $PbMe_2Et_2$, $PbMe_4$ - $PbPr^{\alpha}_4$, $PbMe_3Pr^{\alpha}$ - $PbMe_2Pr^{\alpha}_2$, $PbEt_4$ - $PbPr^{\alpha}_4$, $PbEt_2Pr^{\alpha}_2$, $PbMe_4$ - $PbEt_4$ - $PbPr^{\alpha}_4$, $PbMe_2Bu^{\beta}_2$, and $PbMe_4$ - $PbPh_4$ in presence of a little $AlCl_3$ at 80° alone or in hexane or decahydronaphthalene. $PbMe_3Bu^{\gamma}$ requires 100—130°, and $PbPh_4$ - $Pb(C_6H_4\text{-}p)_4$ requires 200°. 21 other catalysts are listed, notably Al and Pb alkyl halides and metallic halides. Increase in temp. increases the rate of reaction but does not alter the proportions in which products are formed. Solvent may retard the reaction.

VI. Random distribution follows heating $PbMe_2EtCl$, $PbMe_3Cl$ - $PbEt_3Cl$, $PbMe_4$ - $PbEt_3Cl$, $PbMe_4$ - $PbEt_3Br$, or $PbEt_4$ - $PbMe_3Br$ in $COMe_2$ at 60° or hexane at 76° or 80°. Pb alkyl halides themselves act as catalysts.

VIII. In presence of a little $AlCl_3$, the redistribution

reaction leading to random distribution occurs with $\text{HgMe}_2\text{--HgEt}_2$ and HgMeEt at 25° , $\text{SnMe}_4\text{--SnEt}_4$ in pentane at 60° , and $\text{SiEt}_4\text{--SiPr}_4$ at $173\text{--}181^\circ$, but not with $\text{ZnMe}_2\text{--ZnEt}_2$ at $\sim 60^\circ$. Pure HgMeEt is stable at room temp. or 127° . R. S. C.

Reactions of sulphur and vapours of organic compounds at different temperatures. G. D. PALMER, S. J. LLOYD, W. P. McLURE, N. LEMAISTRE, W. S. WARING, and L. W. BACHMAN (J. Amer. Chem. Soc., 1940, **62**, 1005—1006).—Passage of C_6H_6 , PhMe , NH_2Ph , PhOH , PhCl , etc. vapour into S at $240\text{--}260^\circ$ gives resinous S-dyes, but at $260\text{--}300^\circ$ lower yields of solids which are not dyes. At $>300^\circ$ other dyes are formed. High S content is necessary for deep colour. R. S. C.

Velocity of hydrogenation of aromatic and unsaturated hydrocarbons.—See A., 1940, I, 297.

Liquid-phase hydrogenation of *p*-cymene. K. A. KOBE and A. VITTONI (Ind. Eng. Chem., 1940, **32**, 775—777).—*p*-Cymene is most efficiently hydrogenated to *p*-menthane (I), b.p. 171.0° , at 220° /initial H_2 pressure 1000 lb. per sq. in. in presence of Ni catalyst (1%). V.p., d_4 , and n data for (I) for various temp. are also recorded. J. W. S.

Alkylation of benzene with alcohols, boron fluoride, and assistants. N. F. TOUSSAINT and G. F. HENNION (J. Amer. Chem. Soc., 1940, **62**, 1145—1147).— C_6H_6 is alkylated by ROH ($\text{R} = \text{Pr}^a, \text{Pr}^b, \text{Bu}^a, \text{Bu}^b, \text{CHMeEt}, \text{Bu}^r, n\text{-C}_5\text{H}_{11}, n\text{-C}_8\text{H}_{17}, \text{or } n\text{-C}_{12}\text{H}_{25}$) in presence of BF_3 and P_2O_5 , H_2SO_4 , or PhSO_3H . *n*- and *sec*-.Alcohols give *sec*-.alkylbenzenes. $\text{CHMeEt}\cdot\text{OH}$ and Bu^rOH give PhBu^r . Dialkylation gives mainly *p*-compounds. R. S. C.

Trialkylated benzenes and their compounds with aluminium chloride and with aluminium bromide. J. F. NORRIS and J. N. INGRAHAM (J. Amer. Chem. Soc., 1940, **62**, 1298—1301).—Passing HBr into $s\text{-C}_6\text{H}_5\text{Et}_3$ and AlBr_3 gives a compound (I), $2\text{AlBr}_3\cdot 2s\text{-C}_6\text{H}_5\text{Et}_3\cdot \text{HBr}$, m.p. $64\text{--}66^\circ$ (cf. Gustavson, A., 1905, i, 336), stable at 12 mm., giving at 0.002 mm. a compound, $2\text{AlBr}_3\cdot s\text{-C}_6\text{H}_5\text{Et}_3$. With AcCl , (I) gives $1:3:5\text{-}2\text{-C}_6\text{H}_5\text{Et}_3\cdot \text{COMe}$, and with EtBr gives $s\text{-C}_6\text{H}_5\text{Et}_3$ and EtBr . Passage of HCl into (I) causes introduction of $>1\text{ Cl}$. A compound, $2\text{AlCl}_3\cdot 2s\text{-C}_6\text{H}_5\text{Et}_3\cdot \text{HCl}$, m.p. $48\text{--}49^\circ$, is similarly prepared. $s\text{-C}_6\text{H}_5\text{Me}_3$ gives the compound, $2\text{AlBr}_3\cdot 3s\text{-C}_6\text{H}_5\text{Me}_3\cdot \text{HBr}$, m.p. $47\text{--}48^\circ$, stable at 12 mm., but at 0.002 mm. giving the compound, $2\text{AlBr}_3\cdot s\text{-C}_6\text{H}_5\text{Me}_3$. Compounds, (i) $2\text{AlBr}_3\cdot 3\psi\text{-cumene}\cdot \text{HBr}$, (ii) $2\text{AlBr}_3\cdot \text{PhMe}\cdot \text{HBr}$ (stable at 12 mm.; loses PhMe at 0.002 mm.), and (iii) $2\text{AlBr}_3\cdot \text{C}_6\text{H}_6\cdot \text{HBr}$ (loses C_6H_6 at 12 mm.), are prepared. R. S. C.

Influence of organic radicals on para-hydrogen. II. Nature of diradicals. G. M. SCHWAB and N. AGLIARDI (Ber., 1940, **73**, [B], 95—98).—By the para- H_2 method (A., 1938, I, 625), tetraphenyl-*p*-xylylene and *pp'*-diphenylenebis(diphenylmethyl) are found to contain $<0.2\%$ and 9.7% , respectively, of the free radical form. E. W. W.

Steric inhibition of resonance in aromatic nitro-compounds. G. W. WHELAND and A. A. DANISH (J. Amer. Chem. Soc., 1940, **62**, 1125—1127).

—Substitution of 6 Me *o*- to the NO_2 depresses the acidity of $(p\text{-NO}_2\text{-C}_6\text{H}_4)_3\text{CH}$ (cf. A., 1937, II, 92). $1:3:5\text{-C}_6\text{H}_3\text{Me}_2\cdot \text{MgBr}$ and ClCO_2Et give a crude carbinol, converted by $\text{HCl}\text{-Et}_2\text{O}$ into *tri*- $1:3:5\text{-xylylmethyl chloride}$, m.p. 210° , which with Zn dust- $\text{AcOH}\text{-CO}_2$ gives *tri*- $1:3:5\text{-xylylmethane}$, m.p. 108° . Fuming HNO_3 in $\text{Ac}_2\text{O}\text{-AcOH}$ then yields *tri*- $4\text{-nitro-}3:5\text{-dimethylphenylmethane}$ (16%), m.p. 247° , and oily products. Zn dust in boiling AcOH gives the $4:4':4''\text{-(NH}_2)_3\text{-derivative}$, darkens at 190° , decomp. $275\text{--}280^\circ$, also obtained from $1:3:2\text{-C}_6\text{H}_3\text{Me}_2\cdot \text{NH}_2$ (I) by $\text{CH}(\text{OEt})_3$ (gives the *trianilino*-compound, m.p. 179°), followed by (I) and its hydrochloride.

R. S. C.

***pp'*-Diradical of diphenyl, of the triphenylmethyl type.** I. W. THEILACKER and W. OZEGOWSKI (Ber., 1940, **73**, [B], 33—43).—*m*-Tolidine sulphate gives (Sandmeyer) $4:4'\text{-dicyano-}2:2'\text{-dimethyldiphenyl}$, m.p. 113° , b.p. $176^\circ/2\text{ mm.}$, hydrolysed by dil. H_2SO_4 to $2:2'\text{-dimethyldiphenyl-}4:4'\text{-dicarboxylic acid}$, m.p. $330\text{--}332^\circ$, the Et_2 ester, m.p. 70° , b.p. $220^\circ/2\text{ mm.}$, of which with MgPhBr in Et_2O , followed by HCl , yields $2:2'\text{-dimethyl-}4:4'\text{-diphenylenebis(diphenylcarbinol)}$ (I), m.p. 174° or $(+1\text{ AcOH})$ m.p. 121° ; the Et_2 ether, m.p. $199\text{--}200^\circ$ (obtained by use of $\text{EtOH}\text{-HCl}$) [which with dil. HCl in AcOH gives the *glycol acetate*, $2\text{C}_{40}\text{H}_{34}\text{O}_2\cdot \text{C}_4\text{H}_8\text{O}_2$, m.p. 136° and 172° after re-solidification] with dry HCl in AcOH at $50\text{--}60^\circ$ yields $2:2'\text{-dimethyl-}4:4'\text{-diphenylenebis(diphenylmethyl dichloride)}$ (II), m.p. 207° , clearing at 210° , also obtained from (I). When shaken with Hg under CO_2 , (II) in C_6H_6 gives $2:2'\text{-dimethyl-}4:4'\text{-diphenylenebis(diphenylmethyl)}$ (III), m.p. $176\text{--}178^\circ$ (to viscous drops, fluid at $>200^\circ$). This free radical [which is contrasted with the Tschitschibabin hydrocarbon, $4:4'\text{-diphenylenebis(diphenylmethyl)}$ (A., 1907, i, 503)] gives a bluish-green solution (0.01%) in C_6H_6 , which at increasing concn. gives a dichroic solution, green by transmitted and red by reflected light. Air passed through a 4% C_6H_6 solution of (III) gives a peroxide, softens $152\text{--}153^\circ$ (decomp.). The possibility of dimerism of (III) is discussed. E. W. W.

Formation of naphthalene-1:3-disulphonic acid under conditions of direct sulphonation of naphthalene. A. A. TSCHUKSANOVA (Compt. rend. Acad. Sci. U.R.S.S., 1940, **26**, 445).— C_{10}H_8 (16 g.) with conc. H_2SO_4 (65 g.) at 130° for 4 hr. yields the $1:3\text{-}$ (separated as the dichloride) as well as the $1:6\text{-}, 1:7\text{-}, 2:6\text{-}, 2:7\text{-},$ and $1:5\text{-disulphonic acids}$.

A. LI.

Reactions of unsaturated and polynuclear aromatic hydrocarbons with sodium and calcium in liquid ammonia. W. HÜCKEL and H. BRETSCHNEIDER (Annalen, 1939, **540**, 157—189).— C_{10}H_8 and Na in Et_2O with liquid NH_3 at -75° to -65° give a green, then orange-red, and finally a red colour; decomp. with MeOH after ~ 20 min. affords $1:4\text{-dihydronaphthalene}$ (I) (cf. Schlenk *et al.*, A., 1928, 1031). At higher temp. a mixture of (I) and $1:2\text{-dihydronaphthalene}$ (II) results; at the b.p. of NH_3 some (II) is formed. In one experiment nearly pure (II) was obtained. Na in $\text{Et}_2\text{O}\text{-NH}_3$ at -60° converts (I) into (II), whilst (II) and Na in liquid NH_3 at -50° give tetrahydronaphthalene (cf. Wooster

et al., A., 1931, 340). Ca gives similar results. Ph₂ with Na or Ca in liquid NH₃ at -75° to -70° affords 3:4-dihydro-, b.p. 114°/12 mm. (nitrosochloride; nitrolpiperidine, m.p. 194°), converted by Na at -75° into 3:4:5:6-tetrahydro-diphenyl, b.p. 125—126°/14 mm. Terphenyl (prep. described) and Na in liquid NH₃ yield the 3:4-H₂-derivative (III), m.p. 70°, and a hydrocarbon, C₁₈H₁₄, m.p. 152—153° (does not contain a reactive double linking). Catalytic reduction of (III), which reacts readily with Na forming a red compound, gives 4-cyclohexyldiphenyl. (CHPh·CH)₂ reacts fairly readily with Na or Ca affording apparently different products; liquid and solid hydrocarbons are isolated in each case. CH₂Ph₂ gives a blue colour with Ca and the product yields a little of an unsaturated hydrocarbon. 9:10-Diphenylanthracene (IV) and Na in liquid NH₃ give an orange or orange-red solution; decomp. with NH₄Cl or EtOH affords only (IV). Phenanthrene reacts partly with 2 Na or 1 Ca in liquid NH₃ at -75°; 1:2:3:4-tetrahydrophenanthrene, which is probably not the primary reaction product, is isolated. (CH₂·CH)₂ gives C₄H₈ and octadiene. CH. ABS. (b)

Structure of aromatic compounds. III. Action of acetyl chloride on magnesium α - and β -naphthylmethyl halides. N. CAMPBELL, W. ANDERSON, and J. GILMORE (J.C.S., 1940, 819—821). —1-C₁₀H₇·CH₂·MgCl and AcCl give α -di-1-naphthyl- β -methylpropene, m.p. 174—176°, ozonised to 1-C₁₀H₇·CO₂H and 1-C₁₀H₇·CH₂·COMe (2:4-dinitrophenylhydrazones, m.p. 174—176°). 2-C₁₀H₇·CH₂·Br [improved prep. from 2-C₁₀H₇·Me and Br at 240—260° (Hg-vapour lamp)], or, better, 2-C₁₀H₇·CH₂·Cl (I), forms with difficulty a Mg derivative which with AcCl in Et₂O gives α -di-2-naphthyl- β -methylpropene (?), m.p. 184—185°, non-reactive towards alkaline KMnO₄ or Br in CCl₄. CO(CH₂Ph)₂ and MgMeI give CMe(CH₂Ph)₂·OH, which with *o*-C₆H₄(CO)₂O and P₂O₅ at 160° gives CH₂Ph·CMe·CHPh, b.p. 180°/15 mm. (cf. Sabatier *et al.*, A., 1913, i, 717), oxidised to CH₂Ph·COMe. (I) is obtained from SOCl₂ and 2-C₁₀H₇·CH₂·OH (II) [improved prep. by catalytic reduction (Adams Pt, FeCl₃) of the aldehyde]; attempted prep. of (II) from 2-C₁₀H₇·MgI and CH₂O gives 2:2'-(C₁₀H₇)₂. E. W. W.

Dehydrogenation. VI. S. C. SEN-GUPTA (J. Indian Chem. Soc., 1940, 17, 183—188; cf. A., 1940, II, 254).—Hydrindene, cyclopentane-1-acetic-1-carboxylic anhydride, and AlCl₃ in PhNO₂ give β -5-hydrindoyl- α -tetramethylenepropionic acid, m.p. 140—141° (Me ester, m.p. 47—48°, b.p. 210—212°/5 mm.) [oxidised by KMnO₄ to 1:3:4-C₆H₃(CO₂H)₃], reduced by Zn-Hg-conc. HCl to 5- β -1'-carboxy-1'-cyclopentyl-ethylhydrindene, m.p. 104—105°, b.p. 220°/6 mm. 85% H₂SO₄ at 100° then gives 1-keto-6:7-trimethylene-2:2-tetramethylene-1:2:3:4-tetrahydronaphthalene, m.p. 98—99°, oxidised by KMnO₄ to 1:2:4:5-C₆H₂(CO₂H)₄ and reduced by Zn-Hg-HCl to 6:7-trimethylene-2:2-tetramethylene-1:2:3:4-tetrahydronaphthalene, m.p. 64—65°. With Se at 300—320°, later 340—350°, this spiran gives a product, m.p. 149—150° [*s*-C₆H₃(NO₂)₃ compound, m.p. 128—129°], which is probably 2:3-trimethylenanthracene since it differs from 2:3-trimethylenepheneanthrene (I) (syn-

thesis below). Et cyclopentanone-2-carboxylate, HCN, and a drop of aq. KCN at <0° give the cyanohydrin, converted by SOCl₂, first at <0° and then at the b.p., into Et 2-cyano- Δ^1 -cyclopentene-1-carboxylate, b.p. 133—135°/4 mm. Boiling, conc. HCl then yields Δ^1 -cyclopentene-1:2-dicarboxylic acid, m.p. 178°, the anhydride, b.p. 130°/5 mm., of which with AlCl₃ and C₁₀H₈ in PhNO₂ gives mixed keto-acids, m.p. 155—165°, and thence (Clemmensen) mixed 2- α - and 2- β -naphthylmethyl- Δ^1 -cyclopentene-1-carboxylic acids, b.p. 215—220°/5 mm. ZnCl₂ at 180° (85% H₂SO₄ at 100° causes sulphonation) followed by Clemmensen reduction then gives 2:3-trimethylene-1:4-dihydrophenanthrene, m.p. 101—102°, dehydrogenated by So at 300—320° (sealed tube) to (I), m.p. 84° [picrate, m.p. 157°; *s*-C₆H₃(NO₂)₃ compound, m.p. 162—163°]. R. S. C.

Action of perbenzoic acid on aromatic hydrocarbons. H. J. ECKHARDT (Ber., 1940, 73, [B], 13—15).—Carcinogenic hydrocarbons react more readily (cf. Fieser, A., 1938, III, 1022) with BzO₂H than do other hydrocarbons. The reaction is followed iodometrically over a 7—15-day period. Methylcholanthrene > 3:4-benzpyrene > pyrene > benzpyrene-5-aldehyde in reactivity. 5-Nitrobenzpyrene scarcely reacts. Fluorene, phenanthrene, chrysene, and C₁₀H₈ do not react. 6- > 4-Methyl-1:2-benzanthracene > 1:2-benzanthracene > anthracene > 1:2:5:6-dibenzanthracene in activity. E. W. W.

1- β -Styrylacenaphthene. E. B. HERSHBERG and L. M. JOSHEL (J. Amer. Chem. Soc., 1940, 62, 1305—1306).—Acenaphthene-1-aldehyde and CH₂Ph·MgCl in boiling Et₂O-C₆H₆ give 1-acenaphthylbenzylcarbinol (88%), m.p. 109—110°, dehydrated by KHSO₄ at 200° to 1-styrylacenaphthene (71%), m.p. 93.2—94° [dipicrate, m.p. 141.5—143° (decomp.)]. M.p. are corr. R. S. C.

9- and 10-Methyl-1:2-benzanthracene. C. K. BRADSHAW (J. Amer. Chem. Soc., 1940, 62, 1077—1078).—Crude *o*-C₆H₄Cl·CH(OH)·C₁₀H₇- α (prep. from α -C₁₀H₇·MgBr and *o*-C₆H₄Cl·CHO in Et₂O) and red P-I-AcOH-H₂O give 1-*o*-chlorobenzyl-naphthalene, b.p. 189—192°/2 mm., converted by CuCN in C₆H₅N at 250—260° into *o*-1-naphthylmethylbenzonitrile, m.p. 59—60°, b.p. 216—217°/3 mm. With MgMeI in C₆H₆, this gives an imine, hydrolysed to *o*-1-naphthylmethylacetophenone (69%), m.p. 39—40°, b.p. 216—217°/3 mm. Ring-closure by 34% HBr in AcOH gives 86% (29% over-all) of 10-methyl-1:2-benzanthracene. β -C₁₀H₇·MgX (X = Br or I) give similarly 2-*o*-chlorobenzyl-naphthalene, b.p. 203—204°/3 mm., *o*-2-naphthylmethyl-benzonitrile, m.p. 84.5—85.5°, and -acetophenone, b.p. 221°/3 mm., and 9-methyl-1:2-benzanthracene. R. S. C.

Sulphonic acids of pyrene and their derivatives. E. TIETZE and O. BAYER (Annalen, 1939, 540, 189—210; cf. Vollmann *et al.*, A., 1937, II, 450).—Pyrene (I) and ClSO₃H (1 mol.) in C₂Cl₄, first at 0—5° and then at 10—20°/15—20 hr., give pyrene-3-sulphonic acid [Na salt (II), prep. by aq. Na₂SO₄]. 80% HNO₃ and (II) in AcOH at 15—25°/12 hr. afford a nitro-sulphonic acid, reduced (Fe, AcOH) to the NH₂-derivative (readily diazotised and couples

with R salt to a dull violet dye). 93.2% H_2SO_4 and (I) at 0° and then 15°/2 days, followed by NaCl, yield Na_2 pyrene-3:8-disulphonate (III) [also obtained from (II) and 93.2% H_2SO_4 at 5–10°/1 hr.], converted by ~25% (wt.) aq. KOH at 260°/40 atm. into 3:8-dihydroxypyrene (diacetate, m.p. 222–224°); a little pyrene-3:5-disulphonic acid [Ca salt is more sol. than that = (III)] is isolable from the mother-liquors from (III). H_2SO_4 , H_2O and (II) at 15°/1 day followed by CaCO_3 and K_2CO_3 give Na K_2 pyrene-3:5:8-trisulphonate. Treatment of (II) in H_2SO_4 , H_2O with 65% oleum at 20°/15 hr., followed by CaCO_3 and 20% NaCl, affords Na_4 pyrene-3:5:8:10-tetrasulphonate (IV) [also from (I) and Na_2SO_4 in H_2SO_4 , H_2O at 58° followed by 65% oleum at 50–55°], converted by aq. HCl– NaClO_3 into 3:5:8:10-tetrachloropyrene. The successive action of boiling ~20% NaOH, conc. HCl, HCO_2H (neutralisation), and 10% NaCl on (IV) gives Na_3 3-hydroxypyrene-5:8:10-trisulphonate (+ H_2O); aq. 22% NH_3 at 200–210°/18 hr. affords Na_3 3-aminopyrene-5:8:10-trisulphonate. 3-Chloropyrene and Na_2SO_4 in H_2SO_4 , H_2O with 65% oleum at 50–60° yield Na_3 3-chloropyrene-5:8:10-trisulphonate [unaffected by aq. NH_3 (autoclave)]. Fusion of (IV) with NaOH and some H_2O at 130–170° gives Na_2 3:5-dihydroxypyrene-8:10-disulphonate converted by 10% H_2SO_4 at 140–150°/12 hr. into 3:5-dihydroxypyrene (V), darkens in air, m.p. 220° (decomp.) (diacetate, m.p. 154–155°; Me_2 ether, m.p. 177–178°). Zn dust, (IV), and boiling dil. NaOH afford Na_2 pyrene-3:5-disulphonate, which with aq. NaOH at 210–220°/8 hr. yields Na 3-hydroxypyrene-5-sulphonate, with NaOH at 250–260°/15 hr. gives (V), and with HNO_3 – H_2SO_4 at 18°/20 hr. affords 3:5-dinitropyrene-8:10-disulphonic acid [corresponding $(\text{NH}_2)_2$ -compound]. (IV) and ~25% (wt.) NaOH at 240–250°/12 hr. give 3:5:8:10-tetrahydroxypyrene, m.p. 236–238° (Me_4 ether, m.p. 172–173°, not nitratable), which does not couple with diazo-solutions and is oxidised (CrO_3) to a black substance. Many of the above compounds show fluorescence; some are dyes and their behaviour with fabrics is given. CH. ABS. (b)

1-Methylchrysene. L. F. FIESER and L. M. JOSHEL (J. Amer. Chem. Soc., 1940, 62, 1211–1214). — $\alpha\text{-C}_{10}\text{H}_7\text{-CH}_2\text{-CO}_2\text{Na}$ and $o\text{-C}_6\text{H}_4\text{Cl-CHO}$ in Ac_2O at 135° give *o-chloro- α -1-naphthylcinnamic acid*, m.p. 171–172.5°, converted by KOH, first at 200–235° and later 245°, into the lactone (I) (4%), m.p. 244.5–245.5° (decomp.), of *o-hydroxy- α -1-naphthylacetic acid*. $\alpha\text{-C}_{10}\text{H}_7\text{-CH}_2\text{-CO}_2\text{K}$ and $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ in Ac_2O at 125–130° give *o-NO₂-C₆H₄-CH:CH(C₁₀H₇- α)-CO₂H* (68%), m.p. 181.8–182.8° (lit. 173–174°) (and a little *o-NO₂-C₆H₄-CH:CH-CO₂H*), reduced by FeSO_4 or, better, H_2 –PtO₂ in EtOH to the NH_2 -compound (II) (76%). Diazotisation ($\text{C}_5\text{H}_{11}\text{O-NO-H}_2\text{SO}_4\text{-EtOH}$) and subsequent treatment with Cu-bronze in aq. NaH_2PO_4 at 45–50° converts (II) into *chrysene-1-carboxylic acid* (III) (28%), m.p. 225–226° (decomp.) [and a little (I)], the *Me* ester (IV), m.p. 159–160°, of which with $\text{Na-EtOH-C}_6\text{H}_6$ gives *1-hydroxymethylchrysene*, an oil, or with H_2 –Cu chromite in dioxan at 250°/140 atm. gives 58.5%

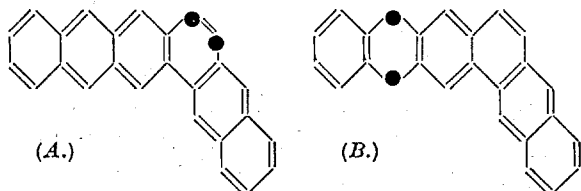
of 1-methyl-3–12:8a:12a-dodecahydrochrysene, m.p. 98.8–99.8° [oxidised by 1:2 $\text{HNO}_3\text{-H}_2\text{O}$ at 195–200° to $\text{C}_6\text{H(CO}_2\text{H)}_5$]. Hydrogenation of (IV) at 160° gives mostly an oily H_2 -derivative. PCl_5 and (III) in boiling C_6H_6 give the acid chloride, which with NH_2Ph in COMe_2 gives the chloroanilide, converted by $\text{SnCl}_2\text{-HCl-Et}_2\text{O-(CH}_2\text{Cl)}_2$ at 0° into chrysene-1-aldehyde. The semicarbazone, m.p. 266–268° (decomp.), thereof with NaOEt-EtOH at 200° gives 17% of 1-methylchrysene, m.p. 116.8–117.6° (picrate, m.p. 141.6–142.4°). M.p. are corr. R. S. C.

Synthesis of 1:12-methylenechrysene and 9:1'-methylene-1:2-benzanthracene from 4:5-methylenepheneanthrene. L. F. FIESER and J. CASON (J. Amer. Chem. Soc., 1940, 62, 1293–1298). — 4:5-Methylenepheneanthrene (I), $(\text{CH}_2\text{-CO})_2\text{O}$, and AlCl_3 in PhNO_2 at 0° (later 5°) give γ -keto- γ -4:5-methylene-1-phenanthryl-*n*-butyric acid (60%), m.p. 207–208° (decomp.) (*Me* ester, m.p. 124.8–125.5°; some isomeride also formed; HF gives a poor yield), reduced (best, crude) by Zn-Hg-HCl-PhMe (and a little AcOH) to γ -4:5-methylene-1-phenanthryl-*n*-butyric acid (55%), m.p. 176.6–177.6° [purified as *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 183.5–184.5°], which with HF gives 90% of 3-keto-1:12-methylene-3:4:5:6-tetrahydrochrysene (II), m.p. 167.5–168.5°. Treatment of (II) with $\text{Al(OPr}^i)_3$ gives a crude carbinol, whence Pd–C at 300–320° gives a little impure 4:5-methylenechrysene (III). Clemmensen–Martin reduction of (II) gives 1:12-methylene-3:4:5:6-tetrahydrochrysene (IV) (59.5%), m.p. 129–129.4°. [With R. C. CLAPP] Hydrogenation (Cu chromite; 160°) of (I) gives 4:5-methylene-9:10-dihydrophenanthrene (85%), m.p. 140.5–141.2°, whence are obtained as above γ -keto- γ -4:5-methylene- (99%), m.p. 224–224.5° (decomp.) (*Na* salt; *Me* ester, m.p. 137.1–137.4°), reduced (H_2 –Cu chromite, very dil. aq. NaOH, 200°, 66%; or Clemmensen–Martin, 44%) to γ -4:5-methylene-, m.p. 154.5–155° (*Me* ester, m.p. 59.3–60°), -9:10-dihydro-2-phenanthryl-*n*-butyric acid (V) and thence (HF) 8-keto-9:1'-methylene- (49%), m.p. 201–203° (decomp.), hydrogenated (≥ 1 atm.) to 9:1'-methylene-3:4:5:6:7:8-hexahydro-1:2-benzanthracene (94.5%), m.p. 83–83.5°. Dehydrogenation by Pd–C at 220° rising to 320° then gives 9:1'-methylene-1:2-benzanthracene. Dehydrogenation of (V) by Pd–C at 200° rising to 265° gives γ -4:5-methylene-2-phenanthryl-*n*-butyric acid (92%), m.p. 167.7–168.0° (purified as *Me* ester, m.p. 36.3–37.3°), which in HF gives 6-keto-1:12-methylene-3:4:5:6-tetrahydrochrysene (VI) (95%), m.p. 173–174°, and thence (H_2 –Cu chromite; EtOH; 160°) 1:12-methylene-3:4:5:6:7:8-hexahydrochrysene (96.5%), m.p. 116.6–117.2°. Dehydrogenation (Pd–C; 220° rising to 270°) then gives (III) (64%), m.p. 172.4–172.9° [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 194–195°; unstable picrate], also obtained (54.5%) similarly from (IV) or (19.5%) (VI). M.p. are corr. R. S. C.

[Nitration of] **3:4-benzpyrene.** H. J. ECKHARDT (Ber., 1940, 73, [B], 15–18). —The conclusion of Fieser *et al.* (A., 1939, II, 364) that 3:4-benzpyrene is nitrated to 5-nitro-3:4-benzpyrene (I) is confirmed. The 9-position is excluded by its ready formation, and

the 10- by the non-identity of 10-amino-3:4-benzopyrene (Windaus *et al.*, A., 1939, II, 106) with the reduction product of (I). With excess of boiling $\text{CrO}_3\text{-AcOH}$, (I) gives 7-benzanthrone-3:4-dicarbonylic anhydride (showing 5- or 8-substitution); $\text{CrO}_3\text{-AcOH}$ under milder conditions yields a mixture which by chromatographic analysis (C_6H_6 , Al_2O_3) gives a dinitro-3:4-benzopyrene, m.p. 294° , probably identical with that obtained by Windaus *et al.* (A., 1937, II, 491), and a product reduced to 5:10- and 5:8-dihydroxy-3:4-benzopyrene diacetate (Vollmann *et al.*, A., 1937, II, 452). E. W. W.

Aromatic hydrocarbons. XXVIII. Hexaphene, a hydrocarbon of the phenene series, and the analysis of its absorption spectrum by the anellation method. E. CLAR (Ber., 1940, 73, [B], 81—86).—By the anellation method (A., 1936, 599, 1102), which is reviewed, it is shown that the hydrocarbon (I) obtained by heating 2:7:1:8- $\text{C}_{10}\text{H}_4\text{Me}_2\text{Bz}_2$ is not 1':2'-anthraceno-1:2-anthracene (II) (cf. A., 1929, 690) but *hexaphene* (cf. A., 1940, II, 124). The absorption spectrum of (II) would resemble that of 2':1'-anthraceno-1:2-anthracene (cf. the spectrum resemblance between 1:2:5:6- and 1:2:7:8-dibenzanthracene). The spectrum of (I) contains three groups of bands, two (α 467, β 357, 339, and 324 $\text{m}\mu$.) corresponding with the *o*-form (A), and one (443, 416, and 392 $\text{m}\mu$.) with the *p*-form (B).



The diquinone from (I) is identified as *hexaphene-5:16:9:14-* (or, less probably, *5:16:8:15-diquinone*). E. W. W.

Synthesis of benzedrine. Q. MINGOIA (Annali Chim. Appl., 1940, 30, 187—198).—Methods of synthesis of benzedrine (I) are reviewed and the classification of sympathomimetic drugs is discussed. The following proposed methods give satisfactory yields of (I): (a) $\text{CH}_2\text{Ph}\cdot\text{COMe}$ (II) is converted into the oxime, which is reduced (Na-Hg-EtOH); (b) (II) is directly reduced in MeOH saturated with NH_3 by H_2 at room temp. and 1.5 atm., using Raney Ni (prep. according to Bougault *et al.*, A., 1939, II, 199) as catalyst; (c) condensation of (II) with $\text{HCO}\cdot\text{NH}_2$ or $\text{HCO}\cdot\text{NHMe}$, followed by hydrolysis (aq. HCl), washing with Et_2O , and fractional distillation of the basic product. The physico-chemical characteristics of, and analytical methods applied to, (I) are described.

F. O. H.

Orientation problems. III. 4:6-Dinitro-*o*-toluidine. A. MCGOOKIN, S. R. SWIFT, and E. TITENSOR (J.S.C.I., 1940, 59, 92—94; cf. A., 1939, II, 255).—1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ could not be chlorinated or sulphonated; nitration by HNO_3 (*d* 1.5), 100% H_2SO_4 , and some H_2O at 80—100° is almost quant. 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ is reduced by aq. NaHS or, less well, Zn dust and aq. NH_4Cl to 4:6:1:2- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Me}\cdot\text{NH}\cdot\text{OH}$, m.p. 110° ; NH_4HS

in aq. dioxan (method: Voris *et al.*, A., 1938, II, 228) gives 30% of 2:6:1:4- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Me}\cdot\text{NH}_2$, whilst $\text{SnCl}_2\text{-HCl}$ in EtOH or dioxan affords (probably) di- and tri-amines. *o*-Toluic acid (I) and HNO_3 (*d* 1.52) at -10° give 4- and 6- NO_2 -derivatives which are converted, as is (I), by 100% $\text{H}_2\text{SO}_4\text{-HNO}_3$ (*d* 1.52) at 20° into 4:6-dinitro-*o*-toluic acid, m.p. 206° (*Et* ester, b.p. $204^\circ/750\text{ mm.}$, m.p. $<15^\circ$; chloride, m.p. 68° , which with NaN_3 in COMe_2 affords the azide, m.p. $237\text{—}239^\circ$, not convertible into the amine); the amide, m.p. 181° , and cold aq. NaOCl give 4:6:1:2- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Me}\cdot\text{NH}_2$ (II), m.p. 155° (cf. lit.). The (II), m.p. 135° , of Brand *et al.* (A., 1913, i, 717) is either a mixture or possibly a hydroxylamine. H. B.

Action of organo-magnesium compounds on araldoximes and their derivatives. Preparation of arylalkylamines of type $\text{NHAr}\cdot\text{CHR}_2$. P. GRAMMATICAKIS (Compt. rend., 1940, 210, 716—718; cf. A., 1937, II, 421).— $\text{CHPh}\cdot\text{N}\cdot\text{OH}$ (I) or $\text{CHPh}\cdot\text{NO}\cdot\text{CO}\cdot\text{NH}_2$ (II) (1 mol.) with MgEtBr (6—10 mols.) in Et_2O gives mainly *N*- α -ethyl-*n*-propylaniline (III), b.p. $114^\circ/14\text{ mm.}$ (hydrochloride, m.p. 161° ; oxalate, m.p. 104° ; picrate, m.p. 107° ; phenylcarbamyl derivative, m.p. 78°), together with some $\text{CPhEt}\cdot\text{NH}$ and NH_2Ph . Similarly, $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ (IV) or $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NO}\cdot\text{CO}\cdot\text{NH}_2$ (V) with MgEtBr gives *N*- α -ethyl-*n*-propyl-*p*-anisidine (VI), b.p. $150^\circ/14\text{ mm.}$ (hydrochloride, m.p. 190° ; oxalate, m.p. 112° ; phenylcarbamyl derivative, m.p. 96°), $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CET}\cdot\text{NH}$, and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (VII). (I) or (II) with MgPhBr gives $\text{NHPH}\cdot\text{CHPh}_2$ (VIII), b.p. $225^\circ/14\text{ mm.}$, m.p. 58° (phenylcarbamyl derivative, m.p. 125°), $\text{CPh}_2\cdot\text{NH}$, and NH_2Ph . (IV) or (V) similarly yields *N*-benzhydryl-*p*-anisidine (IX), b.p. $243^\circ/14\text{ mm.}$, m.p. 81° [hydrochloride, m.p. 194° (decomp.); phenylcarbamyl derivative, m.p. 132°], (VII), and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{NH}$. (III), (VI), (VIII), and (IX) are formed in $>80\%$ yield, together with small amounts of NH_2Ar , by the action of MgEtBr or MgPhBr in Et_2O on $\text{NHAr}\cdot\text{CHO}$. J. L. D.

Molecular rearrangement of tertiary aralkyl-anilines. P. J. DRUMM, W. F. O'CONNOR, and J. REILLY (J. Amer. Chem. Soc., 1940, 62, 1241—1243).— $\text{NPh}(\text{CH}_2\text{Ph})_2\cdot\text{HCl}$ at $200\text{—}220^\circ$ (sealed tube) gives $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, m.p. 36° (hydrochloride, m.p. 219° ; Bz derivative, m.p. 165° ; gives diphenylmethane-4-azo- β -naphthol, m.p. 141°), 2:4:1- $(\text{CH}_2\text{Ph})_2\text{C}_6\text{H}_3\cdot\text{NH}_2$, m.p. 50° [hydrochloride, m.p. 171° ; Bz derivative, m.p. 154° ; gives 2:4-dibenzylbenzene-1-azo- β -naphthol, m.p. 154° , and 2:4:1- $(\text{CH}_2\text{Ph})_2\text{C}_6\text{H}_3\cdot\text{OH}$, b.p. $252\text{—}254^\circ/10\text{ mm.}$ (α -naphthylurethane, m.p. $143\text{—}144^\circ$], and (probably) 2:4:6-tribenzylaniline, m.p. $61\text{—}62^\circ$ (hydrochloride, m.p. 186° ; Bz derivative, m.p. 149° ; gives 2:4:6-tribenzylbenzene-1-azo- β -naphthol, m.p. 146°). Rearrangement, which occurs at $<200^\circ$, cannot proceed by way of an olefine and probably not by way of a free radical since $(\text{CH}_2\text{Ph})_2$ is not obtained, but probably proceeds by way of CH_2PhCl . In conformity with this view, heating $\text{NPh}(\text{CH}_2\text{Ph})_2\cdot\text{HBr}$ in N_2 removes CH_2PhBr , identified as $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{CH}_2\text{Ph}$. R. S. C.

M.p. of *p*-bromoanilides of solid aliphatic acids. D. F. HOUSTON (J. Amer. Chem. Soc., 1940, 62, 1303—1304).—The following m.p. are recorded for $\text{RCO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}\cdot p$: $\text{R} = \text{C}_9\text{H}_{19}$ 101.9°, $\text{C}_{11}\text{H}_{23}$ 106.7°, $\text{C}_{13}\text{H}_{27}$ 110.2°, $\text{C}_{15}\text{H}_{31}$ 113.2°, and $\text{C}_{17}\text{H}_{35}$ 115.2°. R. S. C.

Organic phosphoric acid compounds. VII. Mono- and di-anilidophosphates. F. ZETZSCHE and W. BÜTTIKER (Ber., 1940, 73, [B], 47—49).— $\text{NH}_2\text{Ph}\cdot\text{HCl}$ (I) and POCl_3 at 120—140° give $\text{NHPh}\cdot\text{POCl}_2$ (II), which with further (I) at 145—150° gives $(\text{NHPh})_2\text{POCl}$ (III) (cf. Michaelis *et al.*, A., 1896, i, 344). Cholesterol (IV) and (II) in $\text{C}_6\text{H}_5\text{N}$ at 40—45° yield *dicholesterylphosphoric acid mono-anilide*, $\text{C}_{60}\text{H}_{96}\text{O}_3\text{NP}$, m.p. 196—197°. (IV) and (III) similarly give *monocholesterylphosphoric acid dianilide*, m.p. 182°. With (III), $(\text{CH}_2\text{OH})_3$ gives its *bisdianilidophosphate*, m.p. 180°, glycerol its *trisdianilidophosphate*, m.p. 206°, α -glyceryl *p*-nitrobenzoate its $\alpha'(\text{?})$ -*dianilidophosphate*, m.p. 220°, and sucrose its *octadianilidophosphate*, m.p. 219—220°. Pyrocatechol gives a *bisdianilidophosphate*, m.p. 192°, which is stable to $\text{N}\cdot\text{H}_2\text{SO}_4$ at 60—70° (3 hr.), but when heated with AcOH loses NH_2Ph . E. W. W.

Recognition of carboxylic acids as ureides [acyldiarylcarbamides] with aid of carbodiimides. VII. Detection of α -halogeno-fatty acids. F. ZETZSCHE and G. RÖTTGER (Ber., 1940, 73, [B], 50—56; cf. A., 1940, II, 129).—The following *N*-acyl-*N,N'*-di-*p*-dimethylaminophenylcarbamides are prepared in which the acyl group is: α -chloro-propionyl, m.p. 140° (sinters at 138°), -butyryl, m.p. 146°, -crotonyl, m.p. 136—136.5°, and -phenylacetyl, m.p. 141° (sinters at 138°); mono-*, m.p. 154°, di-, m.p. (impure) 145—146° (partly decomposed by cold COMe_2 or boiling MeOH into a white substance), and tri-chloroacetyl, m.p. 122° (with which di-*p*-dimethylaminophenylcarbamide is obtained) (decomposed by COMe_2 or MeOH); α -bromo-propionyl, m.p. 141°, -n-butyryl, m.p. 142°, -isovaleryl, m.p. 151°, -n-hexoyl, m.p. 137°, - β -dimethylbutyryl, m.p. 124°, -palmityl, m.p. 101°, -tetracosanoyl, m.p. 104°, and -melissyl, m.p. 97—98° (sinters at 94°) [obtained from α -bromo-melissic acid (I), new m.p. 80.5°]; $\alpha\beta$ -dibromo- α -methylbutyryl, decomp. 138° (sinters at 117°), and - β -phenylpropionyl, m.p. 156°; mono-*, decomp. 165—170° (sinters at 153—155°), and tri-bromoacetyl, decomp. (impure) 122° (decomposed by COMe_2 or MeOH), α -iodo-propionyl, m.p. 143°, and -melissyl, m.p. 89° [from α -iodomelissic acid, m.p. 83—85°, obtained from (I) and KI in EtOH]; iodoacetyl, decomp. 165°; β -chloro-propionyl*, m.p. 158°, and -n-butyryl*, m.p. 151°; β -bromo-propionyl*, m.p. 155° (decomp. 156*), -n-butyryl*, m.p. 143°, and - β -phenylpropionyl, decomp. 152° [decomposed by COMe_2 first to a colourless substance, and then to a red substance, m.p. 172° (decomp.)]; hexabromostearyl*, m.p. 153° (sinters at 147°); bromofenchancarboxyl*, m.p. 160°; β -iodopropionyl (II), m.p. 141°. All the above are yellow, except those marked *, which are colourless, and (II), which is yellowish-white. Colour is deepened by α -halogen; Br- and I- have a deeper colour than Cl-compounds. Carbamides of the above type are

not obtained from $\alpha\beta$ -dibromo- $\alpha\beta$ -dimethylbutyric acid or from dibromo- α -cyclogeranic acid. E. W. W.

Preparation of sulphanilamides. M. C. MARQUEZ (Bol. Soc. Quim. Peru, 1940, 6, 17—20).—Preparative details are recorded for sulphanilamide, 2':4'-diaminoazobenzene-4-sulphonamide, and 2-sulphanilamidopyridine. F. R. G.

Sulphonamides and mechanism of their [physiological] action. G. CARRARA and G. MONZINI (Chim. e l'Ind., 1940, 22, 215—216).—The prep. and properties of sulphonamides (I) of therapeutic val. are briefly reviewed. The activity of (I) is related to production of azoxy-groups by oxidation in the organism. Azoxybenzene-4:4'-disulphonamide, m.p. 298—300°, and di(sulphon-2-pyridylamide), m.p. 280—283°, were prepared. F. O. H.

Derivatives of sulphanilamide.—See B., 1940, 566.

Chemotherapy of bacterial infections. I. Substances related to sulphanilamide. Synthesis of *p*-aminobenzylsulphonamide and its derivatives. P. L. N. RAO (J. Indian Chem. Soc., 1940, 17, 227—232).—The following are prepared by condensing $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_2\text{Cl}$ with amines in $\text{C}_5\text{H}_5\text{N}$ and reduction, usually with $\text{Sn} + \text{HCl}$: *p*-nitro- and -amino-benzylsulphonamide, m.p. 168° (Ac, m.p. 212°, valeryl, m.p. 188—189°, hexoyl, m.p. 192—194°, and Bz derivative, m.p. 230—231°); di-*p*-nitro- [using 2 mols. of chloride to 1 NH_3 or 0.5 of $(\text{NH}_4)_2\text{CO}_3$], m.p. 268° (decomp.), and -amino-benzylsulphonamide, decomp. when heated (hydrochloride, m.p. ~275°); *p*-nitro-, m.p. 130—131°, and -amino-benzylsulphonamide, m.p. 172—173° [hydrochloride, m.p. 168—170° (decomp.)]; 2-*p*-nitro-, m.p. 214—215°, and -amino-benzylsulphonamidopyridine, m.p. 185—190° (?) (softens ~120°); *p*-nitro-, m.p. 199—200°, and -amino-benzylsulphonylsulphanilamide, m.p. 162—165° after softening [hydrochloride, m.p. 175—180° (decomp.)]. A. Li.

Oxidation of sulphanilamide and sulpha-pyridine by hydrogen peroxide.—See A., 1940, III, 598.

p-N-Acetylhydroxylaminobenzenesulphonamide and *p*-hydroxylaminobenzenesulphonic acid, both m.p. >300°.—See A., 1940, III, 598.

Oxidation products of sulphanilamide. (Miss) M. K. SEIKEL (J. Amer. Chem. Soc., 1940, 62, 1214—1216).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (I) with $\text{K}_3\text{Fe}(\text{CN})_6\cdot\text{KOH}$ gives 20% of $(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2)_2$ (II), m.p. 314° (decomp.). 30% H_2O_2 in AcOH converts (I) or (II) into azoxybenzene-4:4'-disulphonamide (III) (72%), m.p. 289—290° (decomp.), but in 6*N*- H_2SO_4 (I) gives both (II) and (III). $\text{SnCl}_2\cdot\text{HCl}$ reduces (II) or (III) to (I), but $\text{Na}_2\text{S}_2\text{O}_4$ in 0.2*N*- NaOH gives hydrazobenzene-4:4'-disulphonamide (IV), m.p. 224—224.5°. Oxidation (best, $\text{N}\cdot\text{FeCl}_3$; 90—100% yield) of (IV) gives (II), which is best (46%) prepared by the reactions (I) \rightarrow (III) \rightarrow (IV) \rightarrow (II). With 6*N*- HCl (32 mols.) and 30% H_2O_2 (8 mols.) at room temp., (I) gives 3:5-dichlorosulphanilamide ($\text{SO}_2\cdot\text{NH}_2 = 1$), m.p. 205—205.5°, converted by 75% H_2SO_4 into 2:6:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$. R. S. C.

Reaction of formic acid [with aniline]. T. L. DAVIS and W. P. GREEN, jun. (J. Amer. Chem. Soc., 1940, 62, 1274—1276).—When Br and anhyd. HCO_2H are allowed to react incompletely and treated with NH_2Ph at room temp., some $\text{CO}(\text{NHPh})_2$ and its mixed 4:4'- Br_2 - and 2:4:2':4'- Br_4 -derivatives are obtained. These products are not obtained if all the Br is first allowed to react with the HCO_2H and are probably formed from $\text{CBr}_2(\text{OH})_2$, which is derived from a little $\text{C}(\text{OH})_2$ in equilibrium with HCO_2H . R. S. C.

Interaction of arylhydrazines with halogenated aldehydes. H. IRVING (J.C.S., 1940, 813—817; cf. A., 1933, 1036).— $\text{CHMeBr}\cdot\text{CClBr}\cdot\text{CHO}$ (I) (1 mol.) or $\text{CHMeBr}\cdot\text{CBr}_2\cdot\text{CHO}$ (II) with 2:4:1- $\text{C}_6\text{H}_3\text{Hal}_2\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ (1 mol.) in EtOH affords β -bromo- α -ketobutaldehyde-2:4-dichloro- (III), m.p. 135°, and -dibromo-phenylhydrazone (IV), m.p. 146° (decomp.). $\text{CHMeBr}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})_2$ similarly affords the β -chloro-analogues. (I) or (II) (as hydrates) or $\text{CHMeCl}\cdot\text{CClBr}\cdot\text{CH}(\text{OH})_2$ (1 mol.) and 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ (V) (2 mols.) in boiling MeOH give α -keto- β -methoxybutaldehyde-2:4-dichloro-phenylosazone, also obtained from (III) and (V) (1 mol.) in MeOH. (III) or (IV) and EtOH-NaOEt give the respective 4-hydroxy-1-(2':4'-dihalogenophenyl)-5-methylpyrazole. Equimol. amounts of $\text{CHMeCl}\cdot\text{CCl}_2\cdot\text{CH}(\text{OH})_2$ (VI) and 2:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ in EtOH at <15° afford β -dichloro- α -2:4-dibromobenzeneazo- Δ^2 -butene (VII), m.p. 83°, reduced by Sn-HCl-AcOH to 2:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}_2$, and converted by dry HCl- C_6H_6 into butylchloral-2:4-dibromophenylhydrazone (not isolated). (VII) and dry HCl in EtOH give β -chloro- α -ketobutaldehyde-2:4-dibromophenylhydrazone. (VII) isomerises on refluxing with dry EtOH to α -dichlorocrotonaldehyde-2:4-dibromophenylhydrazone (VIII), m.p. 150° (N-Ac derivative, m.p. 166°); it isomerises when kept alone or, more rapidly, in C_6H_6 , light petroleum, or CHCl_3 , into the isomeride, m.p. 119° (Ac derivative, m.p. 141°), of (VIII). The two forms are regarded as *cis*- and *trans*-isomerides since either Ac derivative and dry Cl_2 in AcOH yield $\alpha\beta\beta$ -tetrachlorobutaldehyde-N-acetyl-2:4-dibromophenylhydrazone, m.p. 108°. (VI) and (V) in dil. HCl-NaOAc, followed by Ac_2O - H_2SO_4 , give α -dichlorocrotonaldehyde-N-acetyl-2:4-dichlorophenylhydrazone (IX), m.p. 153.5° [cf. isomeride, m.p. 122.5° (X) (crystal differences due to habit only)]. (IX) and Sn-HCl-AcOH give 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$. Both isomerides are unimol. in C_6H_6 (f.p.). Isomerism is due to differences in arrangement about the C:C linking since (IX) and (X) with Cl_2 -AcOH give $\alpha\beta\beta$ -tetrachlorobutaldehyde-N-acetyl-2:4-dichlorophenylhydrazone (cf. A., 1930, 324). (X) heated with AcCl (sealed tube) appears to be slowly converted into (IX). A. T. P.

Rate of dissociation of tetraphenylhydrazine.—See A., 1940, I, 325.

Preparation of stable diazo-compounds.—See B., 1940, 513.

Nitrosation of phenols. XVII. *o*-Fluorophenol, and a comparative study of the four

o-halogenophenols. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1940, 810—812).— $\text{o-C}_6\text{H}_4\text{F}\cdot\text{OH}$ and aq. HNO_2 at 0° give 2-fluoro-4-nitroso- (I), m.p. 144° (decomp.), and some 2-fluoro-6-nitro-phenol, m.p. 87°. The quinoneoxime modification of (I) exists only in derivatives. (I) resembles other 4:2:1- $\text{NO}\cdot\text{C}_6\text{H}_3\text{Hal}\cdot\text{OH}$ (A). The $\text{NO}\cdot\text{HSO}_4$ method (A., 1940, II, 12) gives much improved yields of 2-chloro-, new m.p. 145°, -bromo-, new m.p. 156° (decomp.), and -iodo-4-nitrosophenol, new m.p. 162°. 2-Fluoro-, m.p. 89°, -bromo-, m.p. 105°, and -iodo-benzoquinone-4-oxime Me ether, m.p. 120°, are prepared from (A) and Me_2SO_4 -moist K_2CO_3 or (A)-aq. NH_3 -MeOH-AgNO₃ followed by MeI. (A) afford 2-fluoro-, m.p. 195° (decomp.), -bromo-, m.p. 191° (decomp.), and -iodo-benzoquinone-4-oxime-1-p-nitrophenylhydrazone, m.p. 187° (decomp.). Caro's acid and the respective 2-halogeno-4-aminoanisole at 0° yield 2-fluoro-, m.p. 69°, -bromo-, m.p. 85°, and -iodo-4-nitrosoanisole, m.p. 77°. The latter compounds or (A) and CH_2N_2 afford glyoxime NN'-bis-3-fluoro-, m.p. 211°, -bromo-, m.p. 211°, and -iodo-4-methoxyphenyl ether, m.p. 219°, together with some corresponding oxime Me ether (above). NO-compounds have a lower m.p. than the isomeric quinoneoxime. Results of Schiemann *et al.* (A., 1933, 1156) on nitration of $\text{o-C}_6\text{H}_4\text{F}\cdot\text{OME}$ are confirmed. A. T. P.

Dealkylation of alkyl-substituted phenols.—See B., 1940, 515.

Organic molecular compounds. I. Influence of nitro-groups and second substituents on the formation of aromatic-nitroaromatic molecular compounds. I. C. SHINOMIYA (Bull. Chem. Soc. Japan, 1940, 15, 92—103).—In ability to form mol. compounds, $s\text{-(NO}_2)_3 > 2:4\text{-(NO}_2)_2 > \text{NO}_2$ -compounds. The effect of substituents is discussed. The following mol. compounds are described [$A = \alpha$, $B = \beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$; $C = \text{C}_{10}\text{H}_8$; $D = 1:2:4:6\text{-C}_6\text{H}_2(\text{NO}_2)_4$; E = tetryl; $F = 2:4:6:1\text{-(NO}_2)_3\text{C}_6\text{H}_2\cdot\text{OEt}$]: AD , m.p. 137°; BD , 130.5°; C_3D_2 , m.p. 139.5°; A_3E_2 , m.p. 80°; B_2E_3 (of dissociation type); AF_2 , m.p. 68°; BF_2 , m.p. 75.5°; and CF_2 , m.p. 73°. Eutectic points and series of melting and thawing points are also recorded, with phase diagrams. E. W. W.

Organic molecular compounds. II. Influence of nitro-groups and second substituents on the formation of aromatic-nitroaromatic molecular compounds. II. C. SHINOMIYA (Bull. Chem. Soc. Japan, 1940, 15, 137—147; cf. preceding abstract).— $\text{o-C}_6\text{H}_4(\text{NO}_2)_2$ forms no mol. compounds with α - (I) or $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (II). $as\text{-C}_6\text{H}_3(\text{NO}_2)_3$ forms compounds (1:1), m.p. 67°, with (I), (1:1), m.p. 63.5°, and (2:1), m.p. 73°, with (II), and (1:1), m.p. 52.5°, with C_{10}H_8 (III). $2:5:1\text{-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$ forms (1:1) compounds, m.p. 101°, with α - (IV), and, m.p. 96.5°, with $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ (V). $2:3:1\text{-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$ forms (2:3) compounds, m.p. 105°, with (IV), and, m.p. 108°, with (V), but none with (I), (II), or (III). $3:4:1\text{-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$ forms compounds, (1:1), m.p. 96°, with (IV), and, (2:3?), m.p. 83°, with (V), but none with (I), (II), or (III). $3:5:1\text{-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$ forms (1:1) compounds, m.p. 110.5°, with (IV); m.p. 97°, with (V); m.p. 107°, with (I); m.p. 93°, with (II); and, m.p. uncertain,

with (III). Eutectic points etc. and phase-rule diagrams are given. E. W. W.

Preparation of *o*-nitrophenetole from *o*-chloro-nitrobenzene.—See B., 1940, 513.

Migration of the carbamyl radical in *o*-amino-phenol derivatives. L. C. RAIFORD and K. ALEXANDER (J. Org. Chem., 1940, 5, 300—311).—Reduction of *o*-NPh₂·CO₂C₆H₄·NO₂-*o* and its substitution products causes migration of NPh₂·CO from O to N to give the corresponding *o*-carbamidophenol (A). The structures of these compounds are established by preparing them by the direct action of the acid chloride on the required *o*-aminophenol and by showing that the Me ethers obtained from (A) and CH₃N₂ are identical with the products obtained by treatment of the related anisidines with the required carbamyl chloride. Reduction of the related *o*-nitrophenyl phenylmethylcarbamate gives the *o*-aminophenyl derivative. This is also obtained by treatment of *o*-NH₂·C₆H₄·OH with NPhMe·COCl but in this reaction the isomeride is also obtained. Partial hydrolysis of mixed diacyl derivatives containing either of these carbamyl radicals attached to O and another acyl R(Ph)·CO bound to N causes loss of the latter acyl and migration of the former to N. As in many other examples, the heavier acyl is ultimately found attached to N. Migration is not observed when the second radical is ArSO₂. The following are described: *o*-diphenylcarbamidoanisole, m.p. 106—107°; 4-bromo-2-nitrophenyl diphenylcarbamate, new m.p. 137—138°; 4-bromo-2-diphenylcarbamidoanisole, m.p. 155—156°; *o*-nitrophenyl phenylmethylcarbamate, m.p. 111—112°; *o*-phenylmethylcarbamidoanisole, m.p. 77—78°; diacyl derivatives of *o*-NH₂·C₆H₄·OH, *N*-acetyl-*O*-diphenylcarbamyl-, m.p. 150—153°; *O*-acetyl-*N*-diphenylcarbamyl-, m.p. 119—121°; ON-di(diphenylcarbamyl)-, m.p. 184—185°; *N*-diphenylcarbamyl-, m.p. 190—191°; *N*-benzoyl-*O*-diphenylcarbamyl-, m.p. 153—154°; *O*-benzoyl-*N*-diphenylcarbamyl-, m.p. 210—212°; diacyl derivatives of 2:4:1-NH₂·C₆H₃Br·OH, *N*-acetyl-*O*-diphenylcarbamyl-, m.p. 176—178°; *O*-acetyl-*N*-diphenylcarbamyl-, m.p. 117—118°; *N*-diphenylcarbamyl-, m.p. 198°; ON-di(diphenylcarbamyl)-, m.p. 198°; diacyl derivatives of *o*-NH₂·C₆H₄·OH, *O*-phenylmethylcarbamyl-*N*-*p*-toluenesulphonyl-, m.p. 125—126°; *N*-phenylmethylcarbamyl-*O*-*p*-toluenesulphonyl-, m.p. 111—112°; *o*-aminophenyl phenylmethylcarbamate, m.p. 105—106°; *o*-phenylmethylcarbamido-phenol, m.p. 171—172°. H. W.

Phenylisoamyl [γ-phenyl-αα-dimethylpropyl] acetate. K. N. KINZERSKAJA (J. Appl. Chem. Russ., 1940, 13, 222—226).—Ph·[CH₂]₂·CMe₂·OAc (I) is prepared as follows (yields in parentheses): Ph·[CH₂]₂·OH (+ HBr) → Ph·[CH₂]₂·Br (92%) (+ Mg) → Ph·[CH₂]₂·MgBr (+ COMe₂) → Ph·[CH₂]₂·CMe₂·OH (71%) (+ Ac₂O) → (I) (88.5%). R. T.

Dehydration of *cis*- and *trans*-2-phenylcyclohexanols. C. C. PRICE and J. V. KARABINOS (J. Amer. Chem. Soc., 1940, 62, 1159—1161).—*o*-C₆H₄Ph·OH and H₂-Raney Ni in EtOH at 140—150°/135 atm. (not PtO₂ at 70°/3—4 atm.) give *cis*-2-phenylcyclohexanol (I) (75%), m.p. 41—42°, b.p. 140—141°/16 mm. (phenylurethane, m.p. 127.5—128°),

oxidised by CrO₃-AcOH to 2-phenylcyclohexanone, which is reduced by Na-Hg-EtOH to *trans*-2-phenylcyclohexanol (II), m.p. 56—57°. Dehydration of (I) and (II) by boiling H₃PO₄ involves *trans*-elimination. Thus, (I) gives mainly 1-phenyl-Δ¹-cyclohexene, b.p. 126—128°/16 mm. (oxidised by KMnO₄ to COPh·[CH₂]₄·CO₂H), and (II) gives mainly 3-phenyl-Δ¹-cyclohexene (III), b.p. 115—117°/16 mm. (cf. Uspenski, A., 1923, i, 669) [with boiling 5% HNO₃ gives CO₂H·CH₂·CHPh·[CH₂]₂·CO₂H, and with KMnO₄ gives BzOH and (?) BzCO₂H]; small amounts of the other olefine are also formed, probably owing to isomerisation prior to dehydration since (III) is stable to H₃PO₄. M.p. are corr. R. S. C.

Formation of sulphonium compounds from benzyl iodide and organic disulphides. O. HAAS and G. DOUGHERTY (J. Amer. Chem. Soc., 1940, 62, 1004—1005).—R₂S₂ and CH₂PhI with HgI₂ or FeCl₃ in COMe₂ at room temp. give tribenzyl-, m.p. 136—137°, dibenzylethyl-, and dibenzyl-*n*-butyl-sulphonium iodide, all + HgI₂, and tribenzylsulphonium iodide, + FeCl₃, m.p. 142°. A reaction mechanism is postulated, one step of which, (CH₂Ph)₂SI₂ + HgI₂ (in COMe₂) → (CH₂Ph)₃S·HgI₂ + I₂, is realised experimentally. R. S. C.

Alkanolamines. IX. Reducing and hydrolysing action of ethanalamines on dichloronitrobenzenes. C. B. KREMER and A. BENDICH (J. Amer. Chem. Soc., 1940, 62, 1279—1281).—Ability of NH₂·[CH₂]₂·OH (I) and C₆H₃Cl₂·NO₂ to condense is less in absence than in presence of a solvent, reduction, hydrolysis, formation of additive compounds, and reduction of end-products increasing. The latter reactions occur to a greater extent with NH([CH₂]₂·OH)₂ (II) and N([CH₂]₂·OH)₃ (III): 2:5:1-C₆H₃Cl₂·NO₂ (IV) (1 mol.) with (I) (1—2 mols.) alone or with Na₂CO₃ or NaOAc gives 2:4:1-NO₂·C₆H₃Cl·NH·[CH₂]₂·OH (usually the main product), 2:5:1-C₆H₃Cl₂·NH₂ (V), 2:4:1-NO₂·C₆H₃Cl·OH (VI), 2:4:1-NH₂·C₆H₃Cl·NH·[CH₂]₂·OH, and (2:5:1-C₆H₃Cl₂·N)₂, the amounts varying according to the conditions. (II) or (III) with (IV) gives (V), but (VI) is the main product in presence of Na₂CO₃. 3:4:1-C₆H₃Cl₂·NO₂ with (I) (alone or with Na₂CO₃) gives 4:2:1-NO₂·C₆H₃Cl·NH·[CH₂]₂·OH, but with (II) or (III) gives 4:2:1-NO₂·C₆H₃Cl·OH, 3:4:1-C₆H₃Cl₂·NH₂, and 3:4:3':4'-tetrachloroazobenzene, m.p. 195.5° (corr.), the quantities varying according to the conditions. 2:4:1-C₆H₃Cl₂·NO₂ with (I) gives mainly tar, but with (II) 2:4:1-C₆H₃Cl₂·NH₂ (1%) is isolated. 3:5:1-C₆H₃Cl₂·NO₂ with (I) and Na₂CO₃ gives 3:5:3':5'-tetrachloroazobenzene (VII) (60%), m.p. 158.5° (corr.), and 3:5:1-C₆H₃Cl₂·NH₂ (20%), and with (II) gives (VII). R. S. C.

Relative reactivities of organo-metallic compounds. XXX. Co-ordinate compounds in the colour test for organo-metallic compounds. H. GILMAN and R. G. JONES (J. Amer. Chem. Soc., 1940, 62, 1243—1247; cf. A., 1940, II, 239).—CO(C₆H₄·NMe₂-*p*)₂ (I) and MgPhBr in Et₂O-N₂ give a 1:1 additive compound, which regenerates 88% of (I) when hydrolysed but is sufficiently unstable to give enough (*p*-NMe₂·C₆H₄)₂CPh·O·MgBr to yield after hydrolysis the I-AcOH colour test. A similar com-

pound is formed in $C_6H_6-N_2$, but is less stable therein, giving in aq. NH_4Cl only 45% of (I) with 42% of (*p*- $NMe_2 \cdot C_6H_4$) $_2CPh \cdot OH$ (II). Excess of $MgPhBr$ and use of C_6H_6 increase the sensitivity of the colour test. $LiPh$ and (I) give no stable complex in Et_2O or C_6H_6 , but yield 78 and 92.5%, respectively, of (II) without any regenerated (I). The order of decreasing reactivity and increasing tendency to form co-ordinate compounds with ketones is $LiPh$, $MgPhBr$, $GaPh_3$; the relation between these two properties and the responsibility of the latter for effects previously ascribed to steric hindrance are discussed. The forms, m.p. 107—107.5° and 121—122° (cf. lit.), of (II) are obtained. R. S. C.

Chaulmoogra phosphatides. H. ARNOLD (Ber., 1940, 73, [B], 90—94; cf. A., 1939, II, 132).—The Na salt of monohydnocarpoyl- β -glycerophosphoric acid with $AcOH$ and $AgNO_3$ forms the silver ($Ag + Ag_2$) salt, which with $Br[CH_2]_2 \cdot NMe_3Br$ (I) gives *choline monohydnocarpoyl- β -glycerophosphate*, $C_{24}H_{46}O_7NP$. Dihydnocarpoylglycerol gives in the usual way Ag_2 dihydnocarpoyl- β -glycerophosphate. Ag_2 chaulmoogryl-hydnocarpoyl- β -glycerophosphate with (I) gives the *choline ester*, m.p. 170—175° (softens at 70°). The corresponding *choline salt* has m.p. 160—165°. The new compounds appear to have no curative action in leprosy. E. W. W.

Ring-closure of acyclic ureides resulting from elimination of alcohol. Esters of β -phenylalanine-*N*-acetic acid and related compounds. (MISSES) D. A. HAHN, M. J. McLEAN, and M. M. ENDICOTT (J. Amer. Chem. Soc., 1940, 62, 1087—1091).— $CO_2H \cdot CH_2 \cdot NH \cdot CH(CH_2Ph) \cdot CO_2H$ (I) and $HCl-MeOH$ or $-EtOH$ give according to the conditions the *Me* $_2$ ester *hydrochloride*, decomp. 144—145°, *N*-carbomethoxy- (II), m.p. 185—186° (decomp.), stable in H_2O , and *N*-carbomethoxy-methyl- β -phenylalanine hydrochloride (III), m.p. 170—172° (decomp.), hydrolysed in H_2O . With 1 equiv. of $NaOMe-MeOH$ or of aq. $KHCO_3$, (II) gives *N*-carbomethoxymethyl- β -phenylalanine (IV), m.p. 208—210° (decomp.). In boiling H_2O , (III) gives *N*-carbomethoxymethyl- β -phenylalanine (V), m.p. 206—208° (decomp.). NH_3-EtOH converts (IV) or (V) into β -phenylalanine-*N*-acetamide (VI), m.p. 196—197° (decomp.), hydrolysed by dil. HCl to (I). (II) and (III) are sol. in $EtOH$ and H_2O , but (IV) and (V) are insol. *K* of (IV), (V), and (VI) are similar. With $KCNO$ under various conditions, (II), (III), (IV), and (V) give mixtures (cf. A., 1938, II, 279) containing 26—70% of 1- α -carboxy- β -phenylethylhydantoin, m.p. 157—158° (*Na* salt, "anhyd.", decomp. 188—300°, and $+EtOH$, m.p. 60—70°, resolidifies at 91°; *Me* ester, m.p. 105—106.5°), the absorption spectrum of which closely resembles that of 5-benzyl-1-carboxymethylhydantoin. R. S. C.

Optical constants of benzamide, its homologues, and aliphatic amides. M. L. WILLARD and C. MARESH (J. Amer. Chem. Soc., 1940, 62, 1253—1257).—Optical properties of NH_2Bz and 11 Ph-substituted derivatives thereof and of $RCO \cdot NH_2$ ($R = Me, Et, Pr, Bu^a$, and Bu^b) are recorded and may be used for identification. *p*-Ethyl-, m.p. 164.2 \pm 0.5°, *p*-propyl-, m.p. 128.4 \pm 0.5°, *p*-n-, m.p. 121.5 \pm 0.4°,

p-iso-, m.p. 151.2 \pm 0.2°, and *p*-sec.-butyl-, m.p. 117.2 \pm 0.5°, -benzamide are reported. R. S. C.

Synthesis of iodohippuric acids. I. 2:5-, 3:5-, and 3:4-Di-iodohippuric acids. C. J. KLEMME and J. H. HUNTER (J. Org. Chem., 1940, 5, 227—234).—Addition of $AcOH$ to an aq. solution of $o-NH_2 \cdot C_6H_4 \cdot CO_2K$ and $KI-KOI$ gives 2:5:1- $NH_2 \cdot C_6H_3I_2 \cdot CO_2H$, m.p. 210—211.5° (yield 72.2%), converted into 2:5:1- $C_6H_3I_2 \cdot CO_2H$. This with $SOCl_2$ affords 2:5-di-iodobenzoyl chloride, m.p. 93—94.5°, which condenses with aq. $NH_2 \cdot CH_2 \cdot CO_2Na$ to 2:5-di-iodohippuric acid, m.p. 210.5—211°. 3-Iodo-4-aminobenzoic acid, m.p. 203—204°, is obtained by treatment of $p-NH_2 \cdot C_6H_4 \cdot CO_2H$ with ICl in $AcOH$ or (with 2:4:1- $C_6H_3I_2 \cdot NH_2$) with $KI-KOI$ and $AcOH$, and is converted into 3:4:1- $C_6H_3I_2 \cdot CO_2H$, the chloride, m.p. 74—76°, of which is condensed to 3:4-di-iodohippuric acid, m.p. 150—154°, softens at 148°. $o-NH_2 \cdot C_6H_4 \cdot CO_2H$ and ICl in 25% HCl at 80° afford 2:3:5:1- $NH_2 \cdot C_6H_3I_2 \cdot CO_2H$, m.p. 230—232°, whence successively 3:5:1- $C_6H_3I_2 \cdot CO_2H$ (chloride, m.p. 67—68°) and 3:5-di-iodohippuric acid, m.p. 208—209°. H. W.

Halogenation of salicylic acid. L. H. FARINHOLT, A. P. STUART, and D. TWISS (J. Amer. Chem. Soc., 1940, 62, 1237—1241).—2:3:5:1- $OH \cdot C_6H_2Br_2 \cdot CO_2H$ and Br in 60% oleum at $\sim 30^\circ$ give tetra- (I), decomp. $\sim 235-240^\circ$ (*Ac* derivative, m.p. 162.5°), or, if less Br is used, 3:5:6-tri-bromosalicylic acid (II), m.p. 210.5° (*Ac* derivative, m.p. 145°). 2:3:5:1- $OH \cdot C_6H_2Cl_2 \cdot CO_2H$ and Cl_2 in 60% oleum at 80—90° give 3:5:6-trichlorosalicylic acid (III), m.p. 207° (*Ac* derivative, m.p. 129.5°), converted by $Br-60\%$ oleum at $\sim 30^\circ$ into 3:5:6-trichloro-4-bromosalicylic acid (IV), m.p. 213° (*Ac* derivative, m.p. 144°). Attempts to prepare tri-iodo- and other tetrahalogeno-derivatives failed. Structures are proved by decarboxylating with soda-lime; 2:3:4:5-tetrabromo-, m.p. 123° (*acetate*, m.p. 110.5°; *benzoate*, m.p. 133°), and 2:4:5-trichloro-3-bromo-phenol, m.p. 126° (*benzoate*, m.p. 125°), are thus obtained. With $Br-AcOH-H_2O$ at 60°, (I), (II), (III), and (IV) give $C_6H_4Br_5 \cdot OH$, 2:3:4:6:1- $C_6HBr_4 \cdot OH$, 3:4:6:2:1- $C_6HCl_3Br \cdot OH$, and 3:4:6:2:5:1- $C_6HCl_3Br_2 \cdot OH$, respectively. Cl_2 and (III) in 30% $AcOH$ give 2:3:4:6:1- $C_6HCl_4 \cdot OH$. R. S. C.

Oxidation of salicylates in alkaline solution. E. A. BRECHT and C. H. ROGERS (J. Amer. Pharm. Assoc., 1940, 29, 178—183).—The formation of brown-coloured oxidation products from salicylic acid (I) and related compounds was studied. *Na* salicylate (and other phenolic compounds) in 25% $NaOH$ with H_2O_2 slowly forms the Na_2 salt of 2:5-dihydroxy-*p*-benzoquinone; on keeping, this gives a dark brown, amorphous ppt. (I) oxidised by air in slightly alkaline solution or by H_2O_2 gives a brown product ("acid salicylate-brown"), $C_{12}H_6O_6$, containing 3 OH and yielding metallic (*e.g.*, Na_2) salts. F. O. H.

Preparation of depsides by means of azides. III. Action of trimethylgallazide on diphenols. R. O. PERE (Anal. Assoc. Quím. Argentina, 1940, 28,

34—50; cf. A., 1938, II, 491).—3 : 4 : 5 : 1- (OMe)₃C₆H₂·CO·N₃ (I) (2 mols.) in COMe₂ with the appropriate diphenol in N-NaOH gives *o*-, m.p. 155°, *m*-, m.p. 147°, and *p*-phenylene di-(3 : 4 : 5-trimethoxybenzoate), m.p. 218°. 0.5 mol. of (I) yields similarly *o*-, m.p. 172°, *m*-, m.p. 125°, and *p*-hydroxyphenyl 3 : 4 : 5-trimethoxybenzoate, m.p. 154°. With 1 mol. of (I) mixtures are formed; *m*-C₆H₄(OH)₂ affords the highest yield of di-, and *o*-C₆H₄(OH)₂ affords predominately mono-ester.

F. R. G.

Synthesis of carbalkoxystilbenes. R. C. FUSON and H. G. COOKE, jun. (J. Amer. Chem. Soc., 1940, 62, 1180—1183).—Condensation of ArCHO and *p*-CO₂Me·C₆H₄·CH₂Br by Zn dust in C₆H₆ and dehydration of the product by Ac₂O·C₆H₆ gives *Me stilbene* (I) (21%), m.p. 158—159° (dibromide, m.p. 192—193°), 4'-chlorostilbene- (II) (22%), m.p. 161—162° [dibromide, m.p. 202—203° (decomp.)], and 4'-bromostilbene- (20%), m.p. 179—180° (dibromide, m.p. 211—213°), 4-carboxylate. *Me ω*-bromo-*m*-toluate (prep. from *m*-C₆H₄Me·COCl by Br at ~180° and later MeOH), m.p. 46—47°, with *p*-C₆H₄Cl·CHO gives similarly *Me* 4'-chlorostilbene-3-carboxylate (18%), m.p. 110—111° (dibromide, m.p. 175—176°). CH₂PhCl and PhCHO give *trans*-(CHPh)₂ and CH₂Ph₂. *p*-CHO·C₆H₄·CO₂Me and *p*-C₆H₄Cl·CH₂Br give (II) and *di-p*-chlorobenzyl, m.p. 100°. Meerwein's method (A., 1939, II, 262) gives 52% of (I) or 36% of *Et stilbene-4-carboxylate*, m.p. 105—106° (dibromide, m.p. 180—181°), but gives poor yields of Cl-derivatives. *Me ω*-iodo-*p*-, m.p. 76—77°, and *m*-toluate, m.p. 52—53°, are prepared from the corresponding Br-esters by NaI in COMe₂.

R. S. C.

Diarylphthalides derived from dialkylanilines. B. Hoř (Compt. rend., 1940, 210, 701—703).—4'-Methoxy-2'-methyl-5'-isopropylbenzophenone-2-carboxyl chloride with NPhMe₂ and AlCl₃ in cold C₆H₆, followed by treatment with dil. H₂SO₄ and steam-distillation, gives *α*-*p*-dimethylaminophenyl-*α*-(2'-methyl-5'-isopropyl-*p*-anisyl)phthalide, m.p. 207—208° (decomp.). *o*-C₆H₄Bz·CO₂H, *o*-4-anisoyl- and *o*-2 : 5-dimethoxybenzoyl-benzoic acid similarly yield *α*-*p*-dimethylaminophenyl-*α*-phenyl-, m.p. ~160° (decomp.), *p*-anisyl-, m.p. ~76—77°, and -2 : 5-dimethoxyphenylphthalide, m.p. 235° (decomp.), respectively. These phthalides give coloured solutions in conc. H₂SO₄ but not with alkalis unless a phenolic group exists as in *α*-*p*-diethylaminophenyl-*α*-*p*-hydroxyphenylphthalide, m.p. 105—106° (decomp.), prepared from *p*-NEt₂·C₆H₄·CO·C₆H₄·COCl-*o*, PhOH, and AlCl₃.

J. L. D.

Disproportionation in the synthesis of aryloxy-malonic acids. J. B. NIEDERL and R. T. ROTH (J. Amer. Chem. Soc., 1940, 62, 1154—1156).—1 mol. each of NaOAr and CHBr(CO₂Et)₂ in abs. EtOH give OAr·CH(CO₂Et)₂ (I) by condensation, and (OAr)₂C(CO₂Et)₂ and CH₂(CO₂Et)₂ by disproportionation. Use of CHCl(CO₂Et)₂ gives (I). *Phenoxy*-, m.p. 124° (decomp.) (*Et*₂ ester, m.p. 52—53°; *amide*, m.p. 214—215°), *m*-tolyl-*oxy*-, m.p. 138° (decomp.) (*Et*₂ ester, b.p. 154—156°/4 mm.; *diamide*, m.p. 216—217°), *di-m*-tolyl-*oxy*-, m.p. (anhyd.) 148° (decomp.), (+3H₂O) 87° (*Et*₂ ester, b.p. 202—205°/3 mm.), and *p*-nitrophenoxymethyl-, m.p. 142° (decomp.) (*Et*₂

ester, m.p. 50—51°), *malonic acid* are described. Rearrangement of the esters cannot be effected.

R. S. C.

Dinitriles of dicarboxylic acids.—See B., 1940, 515.

Methylenedisalicylic acid and its hexamethylenetetramine salt. B. ODDO (Annali Chim. Appl., 1940, 30, 180—187).—Salicylic acid, 34% CH₂O, and 25% H₂SO₄ are autoclaved for 100 min. at 90—95°; the solid product, when washed with warm H₂O and with C₆H₆, affords methylenedisalicylic acid, m.p. 243° (decomp.) (cf. Clemmensen *et al.*, A., 1911, i, 542), which, directly mixed with (CH₂)₆N₄ or pptd. from COMe₂ solution by C₆H₆, yields (CH₂)₆N₄ methylenedisalicylate (I), softens ~60°, decomp. 120°. (I), the colour reactions of which are given, inhibits potato-oxidase, has bacteriostatic activity, is lethal in rabbits in intravenous doses of 0.85 g. per kg., and, in sufficiently high concns., depresses blood pressure, respiration, and cardiac movement.

F. O. H.

New alkaline fusion procedure. 3-Chloro-4-hydroxy-5-sulphobenzoic acid and its conversion into 3 : 4-dihydroxy-5-sulphobenzoic acid. G. V. MEDOX and N. K. DOBROVOLSKAJA (J. Appl. Chem. Russ., 1940, 13, 191—194).—4 : 3 : 1-

OH·C₆H₃Cl·CO₂H and 10% oleum (30 min. at 84°, then 3 hr. at 145—150°) yield 3-chloro-4-hydroxy-5-sulphobenzoic acid (*K* and *K*₂, +1.5H₂O, salts). This, when heated for 4 hr. at 180° with KOH and paraffin wax, in presence of KI and Cu, yields 3 : 4-dihydroxy-5-sulphobenzoic acid (*K* salt). The paraffin isolates the reaction mass from atm. O₂.

R. T.

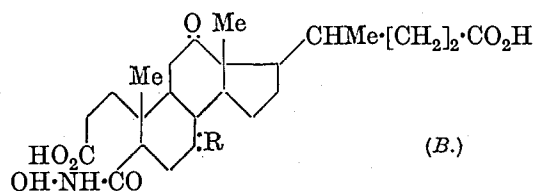
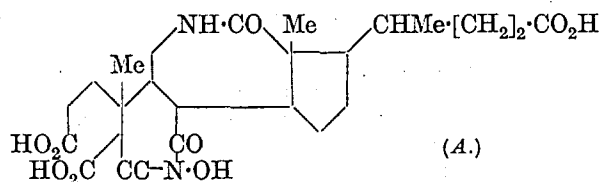
Dicyclic structures prohibiting Walden inversion. dicyclo[2, 2, 2]Octane derivatives with substituents at the bridgehead. P. D. BARTLETT and S. G. COHEN (J. Amer. Chem. Soc., 1940, 62, 1183—1189).—The Br of 9-bromoanthracene-9 : 10-endo-*αβ*-succinic anhydride (I) (Barnett *et al.*, A., 1934, 1102) is unaffected by 30% KOH in 1 : 1 H₂O-EtOH because Walden inversion is impossible; only the *trans*-acid, m.p. 238—240° (barely affected by Ac₂O), is obtained; 10% KOH gives the *cis*-acid, converted at the m.p. or in warm Ac₂O into (I). 9-Bromo-9-methylfluorene (prep. described) reacts readily with EtOH at 25° (half-life period ~5 min.) to give 9-ethoxy-9-methylfluorene, m.p. 82—83°. Na with (I) in EtOH gives ~10% of *trans*-anthracene-9 : 10-endo-*αβ*-succinic acid (II), but Ag or AgNO₃ reacts little if at all. The isomerides of (II) are equilibrated by conc. alkali. 9-Aminoanthracene, softens at 120°, m.p. ~135—140° (cf. lit.), when kept, gives a compound, m.p. 216—217°. 9-Nitro- and 9-acetamido-anthracene with (CH·CO)₂O in boiling xylene give 9-nitro-, m.p. 244—245°, and 9-acetamido-anthracene-9 : 10-endo-*αβ*-succinic anhydride (III), sinters at 257°, m.p. ~268°, respectively, which could not be converted into the 9-NH₂-derivative (IV). With NaOH, (III) gives the *trans*-acid, sinters at 250°, m.p. 253°. *Et* 9-anthrylcarbamate, m.p. 224—225°, gives the 9 : 10-endo-*αβ*-succinic anhydride, m.p. 252—254° (decomp.), hydrolysed by NaOH to (IV), m.p. 260—262° (decomp.). With HNO₃, (IV) gives the 9-OH-compound (yield erratic, up to 65%), m.p. 174—175°, unstable in alkali.

R. S. C.

Tannin, m.p. 165—166° (decomp.), $[\alpha]_D^{27} +17.5^\circ$ in acetone (hexamethyl derivative, m.p. 172—174°), from bark of *Acer spicatum*.—See A., 1940, III, 618.

Steroid-like derivatives [lactams].—See B., 1940, 567.

Reaction of hydroxamic acids. M. SCHENCK and L. WOLF (Ber., 1940, 73, [B], 25—28).—The evolution of gas on treatment with KMnO_4 in 10% NaOH is apparently a general reaction of hydroxamic acids. Acet- and benz-hydroxamic acid give largely N_2O , with some N_2 . The β -acid (A) (cf. A., 1938, II, 99) gives N_2 with 1.5% of O_2 (cf. Schenck, Z.



physiol. Chem., 1939, 262, 47). The oximinoketo-hydroxamic acid, $\text{C}_{24}\text{H}_{36}\text{O}_8\text{N}_2$ (B; R = N·OH), gives N_2 and a substantial proportion of N_2O . The diketohydroxamic acid, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$ (B; R = O), gives N_2 with only a trace of N_2O . Other N-containing bile acid derivatives studied give either no gas or only traces.

E. W. W.

Hydrogenation of benzaldehyde under pressure. G. I. DESCHALIT (J. Appl. Chem. Russ., 1940, 13, 195—197).—PhMe is obtained in 64% yield by hydrogenation of PhCHO (2 hr. at 300—350°/90 atm.).

R. T.

Molecular rearrangements involving optically active radicals. VIII. Wolff rearrangement of optically active diazoketones. J. F. LANE, J. WILLENZ, A. WEISSBERGER, and E. S. WALLIS (J. Org. Chem., 1940, 5, 276—285).—

$d\text{-CH}_2\text{Ph·CHMe·COCl}$ is converted by CH_2N_2 in anhyd. Et_2O at 0°—room temp. into $d\text{-}\beta\text{-phenyl-}\alpha\text{-methyl-ethyl CHN}_2$ ketone (I), $[\alpha]_D^{25} +67.2^\circ$ ($l = 0.5$); the (impure) *l*-isomeride, $[\alpha]_D^{25} -27.9^\circ$ ($l = 0.5$), is hydrolysed by 50% HCO_2H at room temp. to $\delta\text{-phenyl-}\gamma\text{-methylbutan-}\alpha\text{-ol-}\beta\text{-one}$, $[\alpha]_D^{25} -14.03^\circ$ ($l = 0.5$), identified as the *p*-nitrobenzoate, m.p. 73°. When treated with acids in the absence of a catalyst (I) gives an optically active CO-alcohol without appreciable racemisation. With NH_3 in MeOH-AgNO_3 it undergoes a Wolff rearrangement giving a partly racemised (–)- $\beta\text{-benzylbutyramide}$, m.p. 80—81°, whilst with Ag_2O and $\text{Na}_2\text{S}_2\text{O}_3$ in aq. 25% dioxan it yields optically inactive $\beta\text{-benzylbutyric acid (amide, m.p. 83°)}$. $d\text{-CPhMeEt·CO·CHN}_2$ (impure) under the last conditions gives an optically inactive acid.

H. W.

Action of phosphorus pentachloride on $\beta\text{-phenylbenzylideneacetophenone}$. C. R. CONARD

(J. Amer. Chem. Soc., 1940, 62, 1002—1003).— $\text{CPh}_2\text{·CH·COPh}$ and PCl_5 in boiling C_6H_6 give oily 1 : 2-dichloro-1 : 3-diphenylindene (I) (cf. A., 1912, i, 989; for mechanism and analogous reaction with Br, cf. Barré et al., A., 1928, 1009). O_3 converts (I) in CCl_4 into *o*- $\text{C}_6\text{H}_4\text{Bz}_2$ (II). With boiling $\text{EtOH-C}_6\text{H}_6$, (I) gives 2-chloro-1-ethoxy-1 : 3-diphenylindene, m.p. 135.5—136°, ozonised to (II).

R. S. C.

Activation of aluminium chloride in the Friedel-Crafts reaction.—See A., 1940, I, 326.

Condensation of paraformaldehyde with acetomesitylene. R. C. FUSON and C. H. MCKEEVER (J. Amer. Chem. Soc., 1940, 62, 999—1001).—2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{·C(CH}_2)_2\text{·O·MgBr}$ and gaseous CH_2O in Et_2O at 0° give $\beta\text{-hydroxypropiomesitylene}$ (I), b.p. 135—138°/4 mm., which with conc. HCl at room temp. gives $\beta\text{-chloropropiomesitylene}$, m.p. 46—46.5°, obtained also from 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{·CO·CH·CH}_2$ (II) by HCl. Contrary to previous work (A., 1939, II, 162), 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{·COMe}$, paraformaldehyde (III), and K_2CO_3 in MeOH at room temp. give mainly $\beta\text{-methoxy-}\alpha\text{-methylenepropiomesitylene}$ (IV), b.p. 110.5—111°/1.5 mm. (dibromide, m.p. 50.5—51.2°), reduced (H_2 —Raney Ni; MeOH; 2 atm.) to 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{·COPr}^t$. The reaction mechanism is proved by realisation of the following steps: (I) \rightarrow (distillation) (II) \rightarrow ($\text{MeOH-K}_2\text{CO}_3$ or MeOH-conc. HCl) $\beta\text{-methoxypropiomesitylene}$, b.p. 117—117.5°/2.5 mm. (with Br·CCl_4 gives 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{·CO·CHBr·CHMeBr}$) \rightarrow [(III)— $\text{MeOH-K}_2\text{CO}_3$] (IV). K_2CO_3 and (III) in MeOH convert (II) into (IV) and a little $\beta\delta\text{-dimesityl-}\Delta^8\text{-pentadiene}$.

R. S. C.

Acetylretene and reten-6-ol. W. P. CAMPBELL and D. TODD (J. Amer. Chem. Soc., 1940, 62, 1287—1292).—Acetylretene (I) and $\beta\text{-retenol}$ are shown to be C_{33} -derivatives. The retenol (II) obtained from ferruginol and hinokiol (A., 1939, II, 382, 438) is the 6-OH-compound. Retene, AcCl , and AlCl_3 in PhNO_2 , first at –5° and then at 5°, give (I) (45%; mother-liquor yields a product, m.p. 85—89°, and a picrate, m.p. 127—132°), which with 1 : 2 $\text{HNO}_3\text{-H}_2\text{O}$ (later more HNO_3) at 190—200° gives 1 : 2 : 3 : 5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ (III). 6-Methoxy-1-methylphenanthrene gives similarly the 3-Ac derivative (21%), m.p. 126.5—127° (picrate, m.p. 146—148.5°), oxidised by KI_3 in NaOH-dioxan to the 3-carboxylic acid, m.p. 233—235°, which with HNO_3 gives (III). Me $\beta\text{-hydroxydehydroabietate}$ (IV) and Se at 280—285° (later 335°) in N_2 give 68% of reten-6-ol, m.p. 179—180°, identical with (II). Me *O*-methylpodocarpate, AcCl , and AlCl_3 in PhNO_2 , first at 0° and then at 5°, give 80% of the 7-Ac derivative, m.p. 119—119.5°, $[\alpha]_D^{25} +142^\circ$ in EtOH (oxime, m.p. 190—193°), and thence ($\text{MgMeCl-Et}_2\text{O}$) Me *O*-methyl-7- $\alpha\text{-hydroxyisopropylpodocarpate}$, m.p. 148—150°, $[\alpha]_D^{25} +119^\circ$ in EtOH . In boiling AcOH this affords Me *O*-methyl-7-isopropenyl-, m.p. 120.5—121.5°, $[\alpha]_D^{25} +136^\circ$ in EtOH , and thence ($\text{H}_2\text{-PtO}_2\text{-95\% EtOH}$)-7-isopropylpodocarpate (V), m.p. 109—109.5°, $[\alpha]_D^{25} +124^\circ$ in EtOH . Me 6-methoxydehydroabietate [prep. from (IV) by $\text{MgMeCl-Et}_2\text{O}$, followed by Me_2SO_4 ; other methods fail or are erratic], m.p. 65.5—66.5°, $[\alpha]_D^{25} +87^\circ$ in EtOH , differs from (V). Se converts (V) into 6-

methoxyretene, of which 22% is isolated as such and 30% by hydrolysis to (II). R. S. C.

Properties of benzoylmesitoylmethane. R. P. BARNES, C. I. PIERCE, and C. C. COCHRANE (J. Amer. Chem. Soc., 1940, **62**, 1084—1087).—Mesitaldehyde is obtained in 80% yield by hydrogenating (Pd-BaSO₄) mesitoyl chloride in boiling xylene and in 50% yield [with 2:4:6:1-C₆H₂Me₃:CO₂H and -C₆H₂Me₃:CH(OH):CO₂H] by oxidising (KMnO₄-KOH) 2:4:6:1-C₆H₂Me₃:COMe to 2:4:6:1-C₆H₂Me₃:CO:CO₂H and warming the anil thereof with conc. H₂SO₄. 2:4:6:1-C₆H₂Me₃:CO:CHBr:CHPhBr and KOAc in boiling AcOH give 91—92% of *mesityl α-bromostyryl ketone*, m.p. 86°, which reduces KMnO₄, absorbs Br, with MgPhBr gives 2:4:6:1-C₆H₂Me₃:CO:CHBr:CHPh₂, and with hot, conc. KOH-MeOH gives 2:4:6:1-C₆H₂Me₃:CO:CH:CPH:OH (I), m.p. 76—77°, also obtained from (V) (below) by hot HCl-MeOH. (I) is 100% enolic in MeOH, but <1% in CCl₄, gives a Cu derivative, m.p. 221° (decomp.), and with Br in CHCl₃ + CaCO₃ gives β-bromo-α-phenyl-γ-mesitylpropane-αγ-dione (II), m.p. 64—66°, which is 24% enolic and with hot KOAc-AcOH gives mainly (I) with some 2:4:6:1-C₆H₂Me₃:CO:COPh (III). Addition of (I) and then of Br-AcOH to C₅H₅N-H₂SO₄-AcOH gives the ββ-Br₂-derivative, m.p. 107—108°, analogous to (II), converted by KOAc-AcOH into (III). With boiling AcCl, (II) gives *mesityl α-bromo-β-acetoxystyryl ketone*, m.p. 96°, and with boiling KOAc-Ac₂O gives also some 2:4:6:1-C₆H₂Me₃:CO:C(OAc):CPH:OAc. 2:4:6:1-C₆H₂Me₃:CHBr]₂:COPh (IV) and KOAc-AcOH give Ph α-bromo-2:4:6-trimethylstyryl ketone, m.p. 95°, and thence by hot NaOMe-MeOH 2:4:6:1-C₆H₂Me₃:C(OMe):CH:COPh (V), obtained similarly also from (IV). R. S. C.

Diene addition products to diaroylthylenes and their transformation products. R. ADAMS and R. B. WEARN (J. Amer. Chem. Soc., 1940, **62**, 1233—1237; cf. A., 1940, II, 103).—Addition of *trans*-(CH:COAr)₂ (A) (Ar = *p*-C₆H₄Cl, *p*-tolyl, or mesityl) to (CH:CH₂)₂, (CMe:CH₂)₂ (I), or cyclopentadiene in boiling C₆H₆ gives 4:5-di-*p*-chlorobenzoyl-, m.p. 125°, -*p*-toluoyl-, m.p. 127°, and -*mesityl*-, m.p. 204°, -Δ¹-cyclohexene, 4:5-di-*p*-chlorobenzoyl-, m.p. 151°, and -*p*-toluoyl-, m.p. 129°, -1:2-dimethyl-Δ¹-cyclohexene, 4:5-di-*p*-chlorobenzoyl-, m.p. 139°, -*p*-toluoyl-, m.p. 106°, and -*mesityl*-, m.p. 117°, -3:6-endomethylene-Δ¹-cyclohexene. (A) (Ar = mesityl) does not add to (I). The endomethylene products and (II) do not give furans, but with boiling Ac₂O-syrupy H₃PO₄ the other cyclohexenes give 1:2-di-*p*-chlorophenyl-, m.p. 215°, 1:2-di-*p*-tolyl-, m.p. 210°, 1:2-di-*p*-chlorophenyl-4:5-dimethyl-, m.p. 236°, and 1:2-di-*p*-tolyl-4:5-dimethyl-, m.p. 237°, -3:6-dihydroisobenzofuran. By Br-CHCl₃ are obtained 1:2-dibromo-4:5-di-*p*-chlorobenzoyl-, m.p. 181°, -*p*-toluoyl-, m.p. 177°, -*mesityl*-, m.p. 202°, -*p*-chlorobenzoyl-1:2-dimethyl-, m.p. 173°, and -*p*-toluoyl-1:2-dimethyl-, m.p. 184°, -cyclohexane. The Br₂-compounds and a little H₂SO₄ in boiling AcCl (not Ac₂O-H₃PO₄) or, less well, the dihydroisobenzofurans and Br-CHCl₃ at 0° give 4:5-dibromo-1:2-di-*p*-chlorophenyl-, m.p. 179°, and -*p*-tolyl-3:4:5:6-tetrahydroisobenzofuran,

m.p. 166°; the corresponding 1:2-Me₂ compounds are unstable. Addition of Br to the appropriate dihydroisobenzofurans and anhyd. NaOAc in boiling AcOH gives *o*-C₆H₄(COR)₂ (R = *p*-C₆H₄Cl or *p*-tolyl), 4:5-di-*p*-chlorobenzoyl-, m.p. 168—169°, and 4:5-di-*p*-toluoyl-, m.p. 164°, -*o*-xylene, which with boiling NaOH-EtOH, later activated Zn dust in NaOH-EtOH, and finally AcOH-EtOH-Zn dust give 1:2-di-*p*-chlorophenyl-, m.p. 199—200°, -*p*-tolyl-, m.p. 125°, -*p*-chlorophenyl-4:5-dimethyl-, m.p. 213°, and -*p*-tolyl-4:5-dimethyl-, m.p. 186°, -isobenzofuran. With (CH:CO)₂O in C₆H₆ at room temp. (5 min.) these products give 1:4-epoxy-1:4-di-*p*-chlorophenyl-, m.p. 264—266°, -*p*-tolyl-, m.p. 256—258°, -*p*-chlorophenyl-6:7-dimethyl-, forms, m.p. 292—293° and 270—272°, and -*p*-tolyl-6:7-dimethyl-, forms, m.p. 285—286° and 267—268°, -1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride, dehydrated by HCl (gas) in boiling MeOH to 1:4-di-*p*-chlorophenyl-, m.p. 304—305° (block), -*p*-tolyl-, m.p. 293—295° (block), -*p*-chlorophenyl-6:7-dimethyl-, m.p. 321—323° (block), and -*p*-tolyl-6:7-dimethyl-, m.p. 338—340° (block), -2:3-naphthalic anhydride. M.p. are corr.

R. S. C.

Condensations of cyclohexanone and its derivatives with aromatic aldehydes. R. POGGI and (SIGNA.) S. SACCHI (Gazzetta, 1940, **70**, 269—273).—cycloHexanone and *p*-C₆H₄Me:CHO at the b.p. give 2-*p*-tolylidenecyclohexanone (I), m.p. 61—62° {semicarbazone, m.p. 210° (decomp.)}; oxime, m.p. 129.5—130° (softens 125°) [Bz, m.p. 105° (softens 102°)], and Ac derivative, m.p. 116—117.5° (softens 110°)], with 2:6-di-*p*-tolylidenecyclohexanone, m.p. 169—170° (softens 164°), also obtained from (I), which also yields 6-benzylidene-, m.p. 119° (softens 115°), and 6-anisylidene-2-*p*-tolylidene-cyclohexanone, m.p. 149° (softens 147°). E. W. W.

Synthesis of keto-acids. Synthesis of 2-*p*-anisylcyclopentanone-3-carboxylic acid. N. N. CHATTERJEE and G. N. BARPUJARI (J. Indian Chem. Soc., 1940, **17**, 157—160).—*p*-OMe-C₆H₄:CH(OH):CN, m.p. 67°, and CN·CHNa·CO₂Et in EtOH give *Et* αβ-dicyano-β-*p*-anisylpropionate, m.p. 81°, b.p. 225°/5 mm. (and a small amount of an acid, m.p. 226°), which without isolation condenses with Cl[CH₂]₂·CO₂Et to give *Et*₂ αβ-dicyano-α-*p*-anisyl-*n*-butane-βδ-dicarboxylate, b.p. 233—236°/4 mm. This is hydrolysed by boiling 20% H₂SO₄ to α-*p*-anisyl-*n*-butane-αβδ-tricarboxylic acid, m.p. 183° (rapid heating), the *Et*₂ ester, b.p. 205—215°/3 mm., of which with “mol.” Na in boiling C₆H₆ yields *Et*₂ 2-*p*-anisylcyclopentanone-3:5-dicarboxylate, b.p. 200—212° (decomp.)/4 mm., converted by boiling 20% H₂SO₄ into 2-*p*-anisylcyclopentanone-3-carboxylic acid, m.p. 135° [semicarbazone, m.p. 233° (decomp.)]. R. S. C.

Synthesis of keto-acids. Action of sodium ethoxide on diethyl cyclopentanone-2-carboxylate-2-acetate. N. N. CHATTERJEE, B. K. DAS, and G. N. BARPUJARI (J. Indian Chem. Soc., 1940, **17**, 161—166).—*Et*₂ cyclopentanone-2-carboxylate-5-acetate (I), b.p. 160—165°/16 mm., is obtained from *Et*₂ cyclopentanone-2-carboxylate-2-acetate [prep. from *Et* cyclopentanone-2-carboxylate (II) by CH₂Cl·CO₂Et (III) and “mol.” Na in C₆H₆], b.p. 142—

144°/4 mm., by boiling NaOEt-EtOH, probably by way of the open-chain acid (cf. Perkin *et al.*, J.C.S., 1909, 95, 2010). With boiling HCl it gives cyclopentanone-2-carboxylic acid, isolated as semicarbazone, m.p. 198°. With "mol." Na and (III) in C₆H₆ it gives Et₃ cyclopentanone-2-carboxylate-2 : 5-diacetate, b.p. 199—200°/8 mm., converted by boiling, conc. HCl into cyclopentanone-2 : 5-diacetic acid, m.p. 177° (Et₂ ester, b.p. 168—170°/6 mm.). (I) with Cl-[CH₂]₂-CO₂Et (IV) gives similarly Et₃ cyclopentanone-2-carboxylate-5-acetate-2-β-propionate, b.p. 200°/4 mm., and thence cyclopentanone-2-acetic-5-β-propionic acid (V), m.p. 126° (Et₂ ester, b.p. 170°/4 mm.). (II) gives similarly Et₃ cyclopentanone-2-carboxylate-2-β-propionate, b.p. 189°/18 mm., which with boiling NaOEt-EtOH yields Et₂ cyclopentanone-2-carboxylate-5-β-propionate (VI), b.p. 175°/4 mm., converted by Na and (III) in C₆H₆ into Et₃ cyclopentanone-2-carboxylate-2-acetate-5-β-propionate, b.p. 205°/4 mm. [hydrolysed (HCl) to (V)]. (IV) and (VI) give Et₃ cyclopentanone-2-carboxylate-2 : 5-di-β-propionate, b.p. 215°/4 mm., and thence cyclopentanone-2 : 5-di-β-propionic acid, m.p. 122° (Et₂ ester, b.p. 172°/4 mm.).

R. S. C.

Azomethine derivatives of 2-nitro- and 2 : 5- and 2 : 7-dinitro-fluorene. E. A. CALDERÓN and H. PÉREZ (Anal. Asoc. Quím. Argentina, 1940, 28, 5—33; cf. A., 1928, 180).—There is an increase in colour intensity with increase in mol. wt. for the following azomethines which were prepared from the nitrofluorenes with the appropriate NO-compounds in EtOH-KCN: 2-nitro-, m.p. 214°, 2 : 5-dinitro-, m.p. 200°, and 2 : 7-dinitro-fluorenone-p-dimethylaminoanil, m.p. 225°, and the azomethines, m.p. 153°, 280.5°, and 280°, of 4-aminoantipyrine and 2-nitro-, 2 : 5-dinitro-, and 2 : 7-dinitro-fluorenone, respectively. Fluorene did not yield an azomethine under similar conditions.

F. R. G.

Fused carbon rings. XVIII. Further investigations of model substances of the sexual hormone type. V. C. E. BURNOP and R. P. LINSTAD (J.C.S., 1940, 720—727; cf. A., 1938, II, 269).—1-Methyl-2-Δ⁷-butenylcyclohexanol and AcOH (excess)-Ac₂O-H₂SO₄ followed by hydrolysis (20% MeOH-KOH) afford 9-methyldecahydro-β-naphthol (I), epimeric mixture, b.p. 135—138°/19 mm., oxidised by CrO₃-AcOH to cis-2-keto-9-methyldecahydronaphthalene (cf. A., 1937, II, 412). (I) [improved prep. from 2-methyl-1-Δ⁷-butenylcyclohexanol; some (II) is formed] is dehydrated by KHSO₄ to cis-9-methyloctahydronaphthalene (II), which is oxidised by aq. K₂CO₃-KMnO₄ to cis-1-methylcyclohexane-1 : 2-diacetic acid (III), converted by Ba(OH)₂ at 320° into cis-8-methyl-2-hydrindanone (IV). Thus (II) behaves as the Δ²-isomeride (*loc. cit.*). Ozonolysis of (II) in CHCl₃ at 0° or EtOAc at -73° to -76° indicates the presence of some Δ¹-isomeride; hydrolysis (H₂O) of the ozonide, followed by hot aq. NaOH-H₂O₂, affords (III) (40%) and impure (V) (below) (12%) (separable through the Me esters), converted by Ba(OH)₂ at 320° into cis-8-methyl-2-[semicarbazone (formed in cold), m.p. 218—219°] and -1-hydrindanone [semicarbazone (in hot), m.p. 223—224°], respectively. cis-1-Methylcyclohexane-1-carb-

oxylic-2-β-propionic acid (V) has m.p. 108—109° (cf. A., 1938, II, 269). (II) and Pb(OAc)₄-AcOH at 70° afford an acetate, hydrolysed by KOH-MeOH to cis-9-methyl-Δ¹-octahydro-3-naphthol, b.p. 125—130°/12 mm., hydrogenated (PtO₂, EtOH) to the -decahydronaphthol, b.p. 130—132°/12 mm., which is oxidised (CrO₃-AcOH) to cis-3-keto-9-methyldecahydronaphthalene (VI), m.p. 47° (cf. du Feu *et al.*, A., 1937, II, 196). (II) and O₂ + Fe^{II} phthalocyanine at 70° yield cis-3-keto-9-methyl-Δ¹-octahydronaphthalene (VII), b.p. 130°/16 mm. (semicarbazone, m.p. 202—203°), hydrogenated (Pd-EtOH) to (VI). (II) and SeO₂-Ac₂O at 60°, then 100°, afford a compound, b.p. 110—115°/13 mm., hydrolysed by KOH-EtOH to an alcohol, b.p. 120—130°/16 mm., which is oxidised (CrO₃) to (VII). The above oxidations of (II) involve attack at C₃; the Δ²-form present does not react. Al(OPrⁱ)₃-PrⁱOH and (IV) afford cis-8-methyl-2-hydrindanol, probably an epimeric mixture, b.p. 120—122°/21 mm., dehydrated (KHSO₄) to cis-8-methylhexahydroindene (VIII), b.p. 61—62°/19 mm.; aq. KMnO₄ then gives cis-1-methylcyclohexane-1-carboxylic-2-acetic acid. (VIII) and H₂O₂-AcOH at room temp., followed by hydrolysis of the diacetate with KOH-MeOH, afford cis-8-methylhydrindane-1 : 2-diol, b.p. 170—172°/18 mm., dehydrated by KHSO₄ at 200° to the -1-hydrindanone. trans-Δ²-Octahydronaphthalene and Pb(OAc)₄-AcOH at 70° give (mainly) trans-Δ²-octahydro-α-naphthyl acetate, b.p. 131°/12 mm. [hydrolysed by KOH-EtOH to trans-Δ²-octahydro-α-naphthol (IX), b.p. 133—134°/16 mm.], and some diacetate of trans-decahydronaphthalene-2 : 3-diol, m.p. 140°. (IX) and H₂ (PtO₂, EtOH) give the decahydronaphthol, oxidised to not quite pure trans-1-ketodecahydronaphthalene. (IX) and KHSO₄ (or HCl-EtOH) give a hexahydronaphthalene, b.p. 82°/17 mm. (double linkings probably at 2 : 3 and 1 : 9) [maleic anhydride adduct, m.p. 275° (decomp.)], reduced (H₂-PtO₂-EtOH) to (mainly) cis-decahydronaphthalene, and converted by Pd-C at 160°, then 100% H₂SO₄ at 100°, into Na tetrahydronaphthalene-2-sulphonate + cis- and trans-decahydronaphthalene. A. T. P.

Direct introduction of the angular methyl group. R. B. WOODWARD (J. Amer. Chem. Soc., 1940, 62, 1208—1211).—5 : 6 : 7 : 8-Tetrahydro-2-naphthol (3.5 g.) and CHCl₃ in 10% aq. NaOH at 75° give 3-aldehyde-5 : 6 : 7 : 8-tetrahydro-2-naphthol (1.8 g.) and 2-keto-10-dichloromethyl-2 : 5 : 6 : 7 : 8 : 10-hexahydronaphthalene (0.8 g.), m.p. 167.5—168.5° [absorption max. 235 (log ε 4.14) and 329 mμ. (log ε 1.38)], hydrogenated (PtO₂) in MeOH to 2-hydroxy-10-dichloromethyldecahydronaphthalene, m.p. 92.5—93°, sublimes at 64°/high vac. (α-naphthylurethane, m.p. 152.5—153°), which with H₂-Pd-BaSO₄ in 10% KOH-MeOH followed by AcOH-CrO₃ gives 2-keto-10-methyldecahydronaphthalene. R. S. C.

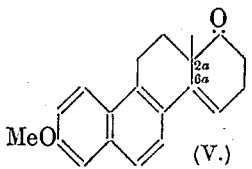
Naphthalene series. I. Synthesis of 5-bromo- and -chloro-1-keto-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. R. H. SIDDIQUI. II. Reactions of the CH₂-CO group. R. H. SIDDIQUI and SALAH-UD-DIN (J. Indian Chem. Soc., 1940, 17, 145—147, 148—151).—I. 3 : 4 : 1-(OMe)₂C₆H₃·CO·[CH₂]₂·CO₂H, m.p. 160—161°, is re-

duced (Clemmensen) to 3:4:1-(OMe)₂C₆H₃[CH₂]₃CO₂H, m.p. 60—61° (lit. 57—59°), which with Br-air in AcOH gives the 6-Br-derivative (I), m.p. 139—140° (lit. 135—136°), and thence by P₂O₅ in boiling moist C₆H₆ 5-bromo-1-keto-7:8-dimethoxy-1:2:3:4-tetrahydronaphthalene (II) (10—15%), m.p. 91—92° [2:4-dinitrophenylhydrazones, m.p. 220—225° (decomp.); semicarbazone, m.p. 215°], hydrolysed by aq. H₂C₂O₄ to (I) (m.p. 142—143°) or by H₂C₂O₄-COMe₂ to (II)]. γ -6-Chloro-3:4-dimethoxyphenylbutyric acid, m.p. 111—112°, and 5-chloro-1-keto-7:8-dimethoxy-1:2:3:4-tetrahydronaphthalene, m.p. 75° (oxime, m.p. 187°; 2:4-dinitrophenylhydrazones, m.p. 239—240°), are similarly prepared.

II. 1-Keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene does not give an oximino-derivative, gives oily CHMe⁺, CH₂⁺, and CH₂:CH:CH⁺ derivatives, 2-CHPh⁺, m.p. 131° (with KMnO₄ gives a little m-hemipinic acid), -o-, m.p. 152°, -m-, m.p. 131°, and -p-OMe-C₆H₄-CH⁺, m.p. 159°, -3':4'-(OMe)₂C₆H₃-CH⁺, m.p. 148°, -2'-furfurylidene, m.p. 151°, -3':4'-CH₂O₂:C₆H₃-CH⁺, m.p. 182°, -CHPh:CH:CH⁺, m.p. 160°, -m-, m.p. 190°, -o-, amorphous, m.p. 152°, and -p-NO₂-C₆H₄-CH⁺, amorphous, m.p. 270°, derivatives. R. S. C.

Fused carbon rings. XIX. Synthesis of tetracyclic compounds of the sexual hormone type. V. C. E. BURNOP, G. H. ELLIOTT, and R. P. LINSTEAD (J.C.S., 1940, 727—735; cf. A., 1938, II, 269; Bachmann *et al.*, A., 1940, II, 225).—Na 1:2:3:4-tetrahydronaphthalene-6-sulphonate and KOH at 200—280° afford 6-hydroxy- and thence (Me₂SO₄-aq. NaOH) 6-methoxy-1:2:3:4-tetrahydronaphthalene (+ some 2-C₁₀H₇-OMe), oxidised by CrO₃-AcOH at 5—10° to 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (I), m.p. 77·5°. (I) and CH₂Br-CO₂Et-Zn wool-C₆H₆ afford a OH-ester, dehydrated by P₂O₅-C₆H₆ to Et 6-methoxy-3:4-dihydro-1-naphthylacetate, b.p. 164—168°/1·5 mm., whence (Bouveault-Blanc) β -6-methoxy-1:2:3:4-tetrahydro-1-naphthylethyl alcohol, b.p. 158—162°/1 mm. (some 6-methoxy-1:2:3:4-tetrahydro-1-naphthylacetic acid is formed), and, by PBr₃-C₆H₆-C₅H₅N, the bromide, b.p. 150—155°/0·7 mm. The latter and CKMe(CO₂Et)₂ in xylene give an ester, hydrolysed by KOH-MeOH to β -6-methoxy-1:2:3:4-tetrahydro-1-naphthylethylmethylmalonic acid, converted at 165°/40 mm. into γ -6-methoxy-1:2:3:4-tetrahydro-1-naphthyl- α -methyl-*n*-butyric acid, which is dehydrogenated by Pd-asbestos (or Pt-C) at 270—280°/40 mm. to γ -6-methoxy-1-naphthyl- α -methyl-*n*-butyric acid, m.p. 87°. P₂O₅-C₆H₆ (or SnCl₄ on the chloride) then gives 1-keto-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthrene (II), m.p. 107°. γ -1-Naphthyl- α -methylbutyric acid and SOCl₂-C₅H₅N give the chloride, converted by SnCl₄-CS₂ at -15°, then at room temp., into 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene (III). Mg Δ^8 -pentenyl bromide (IV) and (I) afford 6-methoxy-1- Δ^8 -pentenyl-1:2:3:4-tetrahydro-1-naphthol, b.p. 168—172°/1·5 mm., which with aq. KMnO₄-Na₂CO₃ gives an acid product, and this when distilled with H₂C₂O₄ yields γ -6-methoxy-3:4-dihydro-1-naphthylbutyric acid, m.p. 133—134° (softens at 127°) (may be partially dehydrogenated) (cf.

Robinson *et al.*, A., 1937, II, 196). (II) and (IV) yield an alcohol, converted by KMnO₄-COMe₂-Na₂CO₃ into an unstable acid (formula given), which with P₂O₅-C₆H₆ gives the 3-keto-10-methoxy-2a-methyl-hexahydrochrysene (V), m.p. 187° (semicarbazone, m.p. 260°), hydrogenated (H₂-PtO₂-AcOH) by addition at C₆ and C_{6a} to the octahydrochrysene, m.p. 212—213° (semicarbazone, m.p. 245°), and thence to the 3-hydroxy-10-methoxy-2a-methyloctahydrochrysene [s-C₆H₃(NO₂)₃ compound, + MeOH, m.p. 155°]. Mg Δ^7 -butenyl bromide and (III) afford a product, dehydrated on distillation (dehydration of higher boiling material can be completed by heating with SiO₂ gel at 180°/10 mm.); chromatographic separation gives mainly 2-methyl-1- Δ^7 -butenyl-3:4-dihydrophenanthrene (VI), b.p. 162°/0·3 mm. [purified through the s-C₆H₃(NO₂)₃ compound, m.p. 65—66°, which on exposure to air and light has m.p. 60—62°, and then (8 days) 80—85°; picrate, m.p. 72—73° (cf. Cohen *et al.*, A., 1936, 62)], and some of the corresponding *tert*-alcohol, C₁₉H₂₂O. Pd-C at 260—265° and then 280—285° converts (VI) into 2-methyl-1-*n*-butylphenanthrene (VII), m.p. 73° [s-C₆H₃(NO₂)₃ compound, m.p. 147—148°; picrate, m.p. 128°]. (VI) and Ac₂O-H₂SO₄-AcOH at 0°, then at room temp., afford a product, b.p. ~152°/0·5 mm. 2-Methyl-1- Δ^7 -butenylcyclohexanol and H₃PO₄ (dehydrated at 235°) in AcOH at room temp., then at 85°, give the acetate, b.p. 125—131°/9 mm., of *cis*-9-methyldecahydro-2-naphthol. (VI) similarly yields 16-methylhexahydrochrysene (VIII) (double linking probably at C₄:C₅) [s-C₆H₃(NO₂)₃ compound, m.p. 123°], best obtained with (VII), from (VI) and P₂O₅ at 140°. (VIII) and Se at 310—330° afford chrysene. (VIII) is not oxidised satisfactorily by KMnO₄, Pb(OAc)₄-AcOH, or SeO₂-Ac₂O; ozonisation and oxidation (alkaline H₂O₂) give an acidic compound, m.p. 165—167° (previous softening). A. T. P.



(V.)

Carbonyl compounds of cyclopentanopolycyclophenanthrene series.—See B., 1940, 566.

Reagent for determining oestrone.—See A., 1940, III, 581.

Steroids. II. 6(α)-Hydroxyprogesterone. M. EHRENSTEIN and T. O. STEVENS (J. Org. Chem., 1940, 5, 318—328).—*Pregnane-3*(β):5:6(*trans*)-triol-20-one 3:6-diacetate, m.p. 215·5—216·5°, [α]_D²⁰ -2·0° in COMe₂, obtained from the triol (A., 1939, II, 554) and boiling Ac₂O, is hydrolysed under defined conditions to the 6-monoacetate, m.p. 222—226°, which is oxidised (CrO₃ in 80% AcOH at room temp.) to *pregnane-5:6*(*trans*)-diol-3:20-dione 6-acetate, m.p. 215—217·5°. This is transformed by HCl in CHCl₃ at <4° into Δ^4 -*pregnen-6*(α)-ol-3:20-dione acetate [*6*(α)-hydroxyprogesterone acetate] (I), m.p. 145—146°, [α]_D²⁰ +89·7° in abs. EtOH, which does not give a yellow colour with C(NO₂)₄ in CHCl₃; its ultra-violet absorption spectrum has a max. at 232 m μ . The corresponding OH-compound appears very unstable and hydrolysis (KOH-MeOH) of (I) seems to yield *pregnane-3:6:20-trione*, m.p. 226·5—230° (impure trioxime, m.p. 165—170°), which is indifferent towards Ac₂O and C₅H₅N

at 100°. (I) has distinct progestational and possibly slight adrenal cortical activity. *Pregnane-3(β):5:6(cis)-triol-20-one 3:6-diacetate*, m.p. 251.5–252°, $[\alpha]_D^{25} +56.6^\circ$ in COMe_2 , is obtained from boiling Ac_2O and the triol (*loc. cit.*). H. W.

Reactions of *o*-benzoquinone.—See B., 1940, 513.

Substituted *p*-quinones and quinols.—See B., 1940, 515.

Hydrogenation of benzoquinone with palladium and platinum catalysts. E. F. ROSENBLATT (J. Amer. Chem. Soc., 1940, 62, 1092–1094).— H_2 -Pt-C reduces $p\text{-O:C}_6\text{H}_4\text{:O}$ in 5% HCl to *cyclohexanol*, but H_2 -Pd-C is similarly ineffective. Hydrogenation occurs only to quinol in neutral solution (EtOH, MeOH) or AcOH, and in MeOH or EtOH Pd-C causes faster reaction than does Pt-C.

R. S. C.

Peroxidase action. II. Oxidation of *p*-toluidine. B. C. SAUNDERS and P. J. G. MANN (J.C.S., 1940, 769–772; cf. A., 1936, 462).—The peroxidase, derived from horseradish or turnips, readily oxidises $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in presence of dil. H_2O_2 -AcOH at p_{H} 4.5 at room temp. to give 4-amino-, m.p. 236°, and 4-*p*-toluidino-2:5-toluquinonebis-*p*-tolylimine, m.p. 183° [H_2SO_4 -EtOH at room temp. give (II) (below)], $\text{NH}(\text{C}_6\text{H}_4\text{Me-}p)_2$, a little ($p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}$)₂ (I), traces (produced by hydrolysis) of 4-amino- and 4-*p*-toluidino-2:5-toluquinone-2-*p*-tolylimine (II), and a substance, m.p. 167°. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ is not formed. H_2O_2 - FeSO_4 -AcOH cause a different reaction; (I) + (II) are among the products formed. Adaptation of Irvine's filter (A., 1915, ii, 832) for continuous elution of a chromatogram is described. A. T. P.

Quinones by the peroxide oxidation of aromatic compounds. R. T. ARNOLD and R. LARSON (J. Org. Chem., 1940, 5, 250–252).—Many aromatic hydrocarbons and their simple derivatives can be oxidised to quinones by 30% H_2O_2 in glacial AcOH, the yields being comparable with those obtained by dichromate oxidation. The greatest val. of the reaction appears to lie in the selective oxidation of alkyl polycyclic derivatives. The following are cited: 1- $\text{C}_{10}\text{H}_7\cdot\text{CHO}$ to 1:4- $\text{O:C}_{10}\text{H}_6\text{:O}$, also obtained from C_{10}H_8 at 80°; durene to duroquinone at 100°; *o*-xylene to *o*-xyloquinone (trace) at 120°; 2- $\text{C}_{10}\text{H}_7\text{Me}$ to 2-methyl-1:4-naphthaquinone (yield 30%) at 80°; 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ to 2:3-dimethyl-1:4-naphthaquinone (yield 78%) under similar conditions; 1:2-benzanthracene in boiling solution to 1:2-benzanthra-9:10-quinone (yield 46%); pyrene in boiling solution to a mixture of pyrenequinones. H. W.

Constitution of vitamin- K_2 . S. B. BINKLEY, R. W. MCKEE, S. A. THAYER, and E. A. DOISY (J. Biol. Chem., 1940, 133, 721–729).—Previous work (A., 1939, III, 853; 1940, III, 146) and that now described indicate that vitamin- K_2 (I) is probably 2-methyl-3- γ - λ - δ - ϵ -hexamethyl- $\Delta^{8,10}$ - ϵ -tetracosahexenyl-1:4-naphthaquinone. Decomp. of the ozonides from dihydrovitamin- K_1 and - K_2 diacetate (II) with Zn dust in Et_2O -AcOH gives 1:4-diacetoxy-2-methyl-3-naphthylacetaldehyde, m.p. 115–115.5° (semicarbazone, m.p. 206–206.5°), oxidised (AcOH- CrO_3) to the -3-naphthylacetic acid, m.p. 209–210° (cf. A.,

1939, II, 513). The ozonide from (II) (1 mol.) also affords COMe_2 (1 mol.) and α -valeraldehyde (5 mols.; similarly obtained in 75% yield from farnesol). The absence of substituents in the benzenoid ring of (I) is shown by oxidation ($\text{COMe}_2\text{-KMnO}_4$) of (II) to $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. (I) does not respond to Craven's colour test (A., 1931, 972). H. B.

Carbonyl constituents of eucalyptus oils. III. Constitution of phellandral. *d*-, *l*-, and *dl*- (synthetic) -Phellandric acids. R. G. COOKE, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1940, 808–810).—Oxidation of *d*-phellandral with AgNO_3 -NaOH gives *d*-phellandric acid, m.p. 144–145°, $[\alpha]_D^{20} +112.8^\circ$ in MeOH (*p*-chloro-, m.p. 78–78.5°, $[\alpha]_D^{20} +71^\circ$ in CHCl_3 , and *p*-bromo-phenacyl esters, m.p. 86°, $[\alpha]_D^{20} +68.1^\circ$ in CHCl_3); the *l*-acid is similarly obtained (*p*-chloro-, m.p. 78–78.5°, $[\alpha]_D^{20} -57^\circ$ in CHCl_3 , *p*-bromo-phenacyl, m.p. 86°, $[\alpha]_D^{20} -52.2^\circ$ in CHCl_3 , and *p*-nitrobenzyl esters, m.p. 56–57°). The *l*-acid in AcOH with $\text{PtO}_2\text{-H}_2$ affords *cis*-hexahydrocuminic acid and in NaOH with Ni- H_2 yields the corresponding *trans*-acid. Bromination of the chloride of the *trans*-acid gives α -bromohexahydrocuminic acid, m.p. 91°, the Et ester of which is debrominated and hydrolysed by Na-MeOH to *dl*-phellandric acid, m.p. 143–144° (*p*-bromophenacyl ester, m.p. 86–86.5°). These results afford additional support for the structure of phellandral as 4-isopropyl- Δ^1 -cyclohexene-1-aldehyde (Δ^1 -tetrahydrocuminal).

F. R. S.

Chloro- and bromo-derivatives of pinane. A. GANDINI (Gazzetta, 1940, 70, 254–265).—Pinane (I) (prep. from *l*-pinene and Pt- H_2 at room temp.) reacts more readily than menthane, camphor, or cineole with halogens. In CHCl_3 with Cl_2 (1 mol.) in H_2O (sunlight) (I) gives 2-chloropinane (II), b.p. 82°/30 mm., $[\alpha]_D^{20} -5.74^\circ$, with ??-dichloropinane, b.p. 106–108°/30 mm., less stable chlorination products, and unchanged (I). With Br (1 mol.), (I) similarly gives 2-bromopinane (III), m.p. 70–72°, b.p. 75–85°/5 mm., and other products. With aq. KMnO_4 , (II) or (III) gives terebinic acid (IV). With KOPh at 150°, (II) or (III) yields mixed pinenes, b.p. 160–165°, hydrogenated to (I). With AgOAc -AcOH at 100°, (III) [or (II)] gives the acetate, b.p. 40–50°/0.1 mm., of an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$, b.p. 83°/14 mm., which is oxidised (Beckmann) to a ketone [probably 2-ketopinane (pinocampnone)] (V), b.p. 72–73°/14 mm. (oxime, b.p. 108–112°/3 mm.; semicarbazone, m.p. 222–230°). With H_2O over activated C at 400°, (V) gives thymol and carvacrol. 5% KMnO_4 oxidises (V) to (IV). E. W. W.

Sesquiterpene alcohol, torreyol. I. K. NISHIDA and H. UOTA (J. Soc. Chem. Ind. Japan, 1940, 43, 64–65b).—The oil (1060 g.), $[\alpha]_D^{25} +38.7^\circ$, from the leaves (528 kg.) of *Torreya mucifera*, S. et Z., contains 0.57% of torreyol, $\text{C}_{15}\text{H}_{26}\text{O}$, m.p. 139–140°, which is probably $\text{CH}_2\text{-CHMe-CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}(\text{CMe}_2)\text{-CH-CH}_2\text{-CMe-OH}$. It gives colour reactions for $\text{C}\cdot\text{C}$, a cryst., hygroscopic acetate, contains a *tert.* OH, with H_2 -Pd-black in EtOH gives a H_2 -derivative (I), m.p. 106–107°, $[\alpha]_D^{25} -10.79^\circ$, with Se gives cadalene, with boiling HCO_2H gives torreyene, $\text{C}_{15}\text{H}_{24}$, b.p. 89–90°/1 mm., $[\alpha]_D^{25} +46.67^\circ$

(hydrogenated to cadinene), and with $\text{HCl-Et}_2\text{O}$ gives a compound, $\text{C}_{15}\text{H}_{26}\text{Cl}_2$, m.p. 118–119°. Boiling HCO_2H dehydrates (I) to *dihydrotorreyene*, b.p. 90–91°/1 mm., $[\alpha]_D^{25} +13.05^\circ$. R. S. C.

Constitution of calameon. H. BÖHME (Arch. Pharm., 1940, 278, 1–7).—Calameon (I) is a singly unsaturated, *diterp.*, dicyclic sesquiterpene alcohol of the cadalene (II) series. The presence of a double linking in (I) is established by oxidation with $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and of 2 OH by Zerevitinov's method. (I) is hydrogenated (Pd-C-MgO in 96% EtOH) to *dihydrocalameon*, m.p. 133°, and converted by boiling 50% H_2SO_4 into calamene, b.p. 137–139°/12 mm., $\alpha_D^{17} -6.60^\circ$ ($l = 0.5$), which is dehydrogenated by S at 200–260° to (II). H. W.

Triterpene group. VII. Minor triterpenoid constituents of *Manila elemi* resin. (Miss) I. M. MORICE and J. C. E. SIMPSON (J.C.S., 1940, 795–799).—A new and standardised method is described for the prep. of brein (I) from the resin, depending on fractional elution from activated Al_2O_3 , followed by formylation. The *di-formate* of (I) has m.p. 220–221°, $[\alpha]_D^{25} +67^\circ$, hydrolysed to (I), m.p. 221–222°, $[\alpha]_D^{25} +63.5^\circ$ (diacetate, m.p. 197–198°, $[\alpha]_D^{17} +70^\circ$; dibenzoate, m.p. 209–210°, $[\alpha]_D^{17} +58^\circ$). From the mixed alcohols, there have been isolated *maniladiol*, $\text{C}_{30}\text{H}_{50}\text{O}_2$, m.p. 220–221°, $[\alpha]_D^{19} +68^\circ$ (*di-formate*, m.p. 186–187°, $[\alpha]_D^{17} +84^\circ$; *diacetate*, m.p. 193–194°, $[\alpha]_D^{25} +80^\circ$; *dibenzoate*, m.p. 233–234°, $[\alpha]_D^{17} +63.5^\circ$), and ψ -taraxasterol (*formate*, m.p. 219–221°, $[\alpha]_D^{17} +51^\circ$); it is probable that the latter is produced during the working up of the resin by cyclisation of a tetracyclic isomeride. All $[\alpha]$ are in CHCl_3 . F. R. S.

Essential oil of *Evodia littoralis*.—See B., 1940, 494.

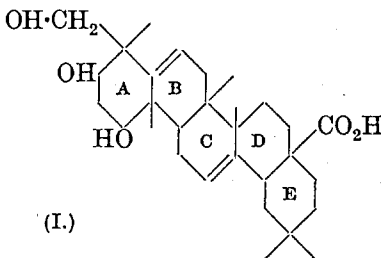
Oleo margosa from *Melia azadirachta*, neem oil. I. Isolation of the constituents of the oil. M. QUDRAT-I-KHUDA, S. K. GHOSH, and A. MUKHERJEE (J. Indian Chem. Soc., 1940, 17, 189–194).—Distillation of the commercial oil, $d_4^{25} 0.9108$, $n_D^{25} 1.46185$, I val. 69.56, sap. val. 198.8, in steam gives *neemola*, $\text{C}_{15}\text{H}_{30}\text{O}_3\text{S}$, b.p. 156–158°/118 mm. (nauseous odour; decolorises Br; sol. in aq. Na_2CO_3). The non-volatile portion yields to hot H_2O a bitter glucoside, *margosin*, $\text{C}_{28}\text{H}_{48}\text{O}_{10}$, m.p. 193–195°, and after hydrolysis (KOH-aq. EtOH) *neem acid-A*, $\text{C}_{14}\text{H}_{28}\text{O}_2$, m.p. 67°, -B, $\text{C}_{16}\text{H}_{32}\text{O}_2$, m.p. 55° (also present in the volatile portion), -C, $\text{C}_{15}\text{H}_{28}\text{O}_2$, m.p. 47–48°, b.p. 189–190°/4 mm. {Me ester, b.p. 177°/3 mm. [*dibromide*, b.p. 230° (decomp.)/4 mm.]; olefinic}, and -D, $\text{C}_{18}\text{H}_{32}\text{O}_2$, m.p. 31–33°, b.p. 194–195°/4 mm. {Me ester, b.p. 183°/3 mm. [*dibromide*, b.p. 223° (decomp.)/4 mm.]; cycloparaffinoid}. R. S. C.

Identity of obaculactone, evodin, and dictamnolactone with limonin. M. S. SCHECHTER and H. L. HALLER (J. Amer. Chem. Soc., 1940, 62, 1307–1309).—These substances are identical, have m.p. (from $\text{COMe}_2\text{-EtOH}$) 299–300° (corr.), (from AcOH) 297–298° (corr.), $[\alpha]_D^{20} -129^\circ$ in COMe_2 , $+32.6^\circ$ in N-KOH-EtOH , have the composition, $\text{C}_{26}\text{H}_{30}\text{O}_8$, contain no Oalk, CO, or OH, and are hydrogenated to a mixture. R. S. C.

Alcohol, $\text{C}_{30}\text{H}_{48}\cdot\text{OH}$, m.p. 110–112° (decomp.) (dibromide, m.p. 135–140°; acetate, m.p. 165–167°; benzoate, m.p. 205–206°), from cotton plant latex.—See A., 1940, III, 618.

Sterols. XCVIII. Conversion of isosarsapogenin (smilagenin) into tigogenin. R. E. MARKER, E. ROHRMANN, and E. M. JONES (J. Amer. Chem. Soc., 1940, 62, 1162–1163).—The “iso”-configuration of the side-chain of tigogenin (I) (cf. A., 1940, II, 184) is confirmed. *isoSarsapogenone* and Br-HBr-AcOH give the Br_2 -derivative, m.p. 184–188° (decomp.), which in boiling $\text{C}_5\text{H}_5\text{N}$ yields *bromo- $\Delta^{4:5}$ -dehydroisosarsapogenone*, m.p. 200–205° (decomp.) [*pyridinium salt*, m.p. 245–246° (decomp.)]. Na-EtOH then gives (I). Neotigogenin is isomerised to (I) by boiling HCl-EtOH . R. S. C.

Sapogenins. IX. Occurrence and constitution of bassic acid. B. J. HEYWOOD and G. A. R. KON (J.C.S., 1940, 713–720).—Bassic acid (I) (cf. Heywood *et al.*, A., 1939, II, 436) has been isolated from the seeds of all except two of the Sapotaceae examined, and appears to be the characteristic sapogenin of the order. Me bassate occurs in two forms, α , m.p. 214–215°, $[\alpha]_D +64^\circ$, and β , m.p. 220°, $[\alpha]_D +55.5^\circ$, both of which give the same acetyl derivative (cf. van der Haar, A., 1930, 92). This compound is oxidised ($\text{AcOH-H}_2\text{CrO}_4$) to an *acetyl compound*, m.p. 181–183°, hydrolysed to *Me dehydrobassate*, m.p. 202–203.5° (*semicarbazone*, m.p. 210–213°), and possessing no reducing properties; the OH having undergone oxidation must be secondary. The Br-lactone (*acetyl compound*, m.p. 205–206°) with Zn-AcOH gives a hydroxy-lactone, m.p. 236°, and is oxidised ($\text{AcOH-H}_2\text{CrO}_4$) to a *triketone*, $\text{C}_{29}\text{H}_{39}\text{O}_5\text{Br}$, m.p. 245° (decomp.) [*mono-2:4-dinitrophenylhydrazone*, m.p. 286–288° (decomp.)]; 2:4-dinitrophenylhydrazone of Me ether, m.p. 294–295° (decomp.)]; the absorption spectra indicate two conjugated double bonds. With Br in AcOH , the triketone affords a *dibromo-triketone*, $\text{C}_{29}\text{H}_{36}\text{O}_5\text{Br}_2$, m.p. 229° (decomp.). Oxidation of the β -ester with Cu-bronze



yields a *diketone*, $\text{C}_{30}\text{H}_{42}\text{O}_4$, b.p. 130–140°/0.00064 mm., which is oxidised to a neutral product [2:4-dinitrophenylhydrazone, m.p. 274–276° (decomp.)] and reduced ($\text{PtO}_2\text{-H}_2$) to a H_4 -compound, $\text{C}_{30}\text{H}_{46}\text{O}_4$, m.p. 218–219°. From the evidence it is deduced that the third OH of (I) is placed on $\text{C}_{(4)}$ in ring A and one of the double bonds is in ring B between $\text{C}_{(6)}$ and $\text{C}_{(7)}$. The complete formula for (I) is suggested. F. R. S.

Resin acids. III. Primary resin acids isolated from Russian pine resin. V. N. KRESTINSKI, S. S. MALEVSKAJA, N. F. KOMSCHILOV, and E. V. KAZEEVA (J. Appl. Chem. Russ., 1939, 12, 1840–1847).—*Pinus sylvestris* resin is a mixture of isomeric acids, $\text{C}_{19}\text{H}_{29}\cdot\text{CO}_2\text{H}$, three of which have been identified as *d*-(I) and *l*-pimaric acid (II) and α -sapienic

acid (III); the presence of β -pimaric acid is uncertain. (I) and (II) are present in the resin of *P. maritima* and *palustris* and *Picea excelsa*. (II) and (III) are converted into abietic acid by heating at 200–210° (1–1.5 hr.); under these conditions (I) is recovered unchanged. (I) and (II) have very similar absorption spectra. R. T.

Pharmacologically valuable components of Indian hemp. II. "Cannabinum tannicum" and modified determination of tannin. K. W. MERZ and K. G. BERGNER (Arch. Pharm., 1940, 278, 97–109).—"Cannabinum tannicum," formerly used as a hypnotic, is not the tannate of an alkaloid and does not contain appreciable amounts of other substances of pharmacological interest. Two samples consisted essentially of mixtures of K and Mg tannate with lactose. Traces of chlorophyll, choline, and an odoriferous glucoside containing coumarin were also present with hemp resin in pharmacologically significant amount. Attempts to prepare a "cannabinum purum" by decomp. of cannabin tannate with ZnO were unsuccessful. H. W.

Vitamin-B₁. XIX. Derivatives of γ -aceto-propyl alcohol. J. R. STEVENS and G. A. STEIN (J. Amer. Chem. Soc., 1940, 62, 1045–1048; cf. A., 1939, II, 289).— α -Chloro- α -acetobutyrolactone (I) and HCl (12 c.c. in 410 c.c. of H₂O) at 100° give 3-chloro-2- γ -chloro- δ -keto-n-amyloxy-2-methyltetrahydrofuran (II) (62%), b.p. 111–112°/1 mm. [previously (A., 1936, 1394) reported as (III)], and some γ -chloro- δ -keto-n-pentan- α -ol (III), b.p. 20–24°/0.003 mm. Distillation at 1 mm. dehydrates (III) to (II). Hydrolysis of (II) to (III) is easy; e.g., it occurs in dil. aq. solution at 60° as shown by cryoscopy and by isolation of (III); with HCS·NH₂·H₂O, (II) gives 4-methyl-5- β -hydroxyethylthiazole. COMe·[CH₂]₃·OH (IV) and Br·H₂O at 24–30° give mainly COMe·CHBr·[CH₂]₂·OH, but after distillation only 3-bromo-2- γ -bromo- δ -keto-n-amyloxy-2-methyltetrahydrofuran, b.p. 40° (bath)/0.008 mm., is obtained. This is readily hydrolysed by H₂O but the alcohol formed cannot be isolated. (IV) is more stable; when repeatedly distilled at 10 mm., it gives 2- δ -keto-n-amyloxy-2-methyltetrahydrofuran (V), b.p. 110–112°/12 mm. [gives the semicarbazone of (IV)], the reaction being catalysed by a trace of HCl. The structure of the ethers is proved as follows. With MgMeI, (V) gives (1 mol. consumed; no active H) (IV) and OH·CMe₂·[CH₂]₃·OH, indicating addition at the CO. With NHPH·NH₂ (excess) in Et₂O, (III) gives NHPH·NH₂·HCl and 3-chloro-2- δ -benzeneazo- Δ^2 -pentenyl-2-methyltetrahydrofuran, m.p. ~85° (decomp.). (III) gives ~ twice as much I after as before hydrolysis. 3-Chloro-2-ethoxy-2-methyltetrahydrofuran (does not react with NHPH·NH₂ or NaOI) is prepared from (I) by H₂SO₄–80% EtOH at 40–50° or similarly from (III) and with aq. HCl (p_H 3) gives (III). R. S. C.

Velocity of transformation of acetonedioxalic ester into chelidonic ester.—See A., 1940, I, 297.

Chalkones. Reactions of o-hydroxyphenyl 6-methoxy-2 : 3-benzostyryl ketone and of some derivatives. B. G. ACHARYA, R. C. SHAH, and T. S.

WHEELER (J.C.S., 1940, 817–819).—2 : 1-OMe·C₁₀H₆·CHO (I) (modified prep.), o-C₆H₄Ac·OH (II), and aq. NaOH–EtOH at 60° afford o-hydroxyphenyl 6-methoxy-2 : 3-benzostyryl ketone (III), m.p. 142° (Ac derivative, m.p. 107°). 2 : 1-OH·C₁₀H₆·CHO (IV) and o-C₆H₄Ac·OMe (V) similarly yield o-anisyl 6-hydroxy-2 : 3-benzostyryl ketone, m.p. 153°. (II) and (IV), or (I) and (V), give o-hydroxyphenyl 6-hydroxy-, m.p. 140° [also from (III)–AlCl₃ at 125°], or o-anisyl 6-methoxy-2 : 3-benzostyryl ketone, m.p. 103°, respectively. (II), (IV), and HCl–EtOAc for 4 days yield 2'-hydroxy-5 : 6-benzoflavylum chloride, m.p. 215–220° (decomp.). (III) and H₂O₂ in aq. KOH–EtOH afford 2-(2'-methoxy-1'-naphthyl)-3-chromonol (VI), m.p. 239° (Ac derivative, m.p. 173°). (III), CH₃Ac·CO₂Et, and NaOEt–EtOH give Et 5-o-hydroxyphenyl-3-(2'-methoxy-1'-naphthyl)- Δ^5 -cyclohexenone-2-carboxylate, m.p. 187° (semicarbazone, m.p. 172°; oxime, m.p. 212°). (III), cyclohexanone, and Na–Et₂O give 2- β -o-hydroxybenzoyl- α -2'-methoxy-1'-naphthylethylcyclohexanone, m.p. 178°. (III) and Br·CHCl₃ yield o-hydroxyphenyl $\alpha\beta$ -dibromo- β -2-methoxy-1-naphthylethyl ketone, m.p. 152° (decomp.), converted by EtOH into the α -bromo- β -ethoxy-analogue (VII), m.p. 179°, or by aq. KCN into 2-(2'-methoxy-1'-naphthyl)chromone, m.p. 178° (cf. Nadkarni et al., A., 1938, II, 18). (VII) and aq. NaOH–EtOH at 60° give 1-(2'-methoxy-1'-naphthylidene)coumaran-2-one (VIII), m.p. 178° (2 : 4-dinitrophenylhydrazones, m.p. 238°) (characteristic reactions of keto-ethylenic group not affected by cyclic linking), converted by Br·CHCl₃ into the dibromide, m.p. 158° [aq. KOH–EtOH gives (VI)], and thence by EtOH into 1-bromo-1-(ethoxy-2'-methoxy-1'-naphthylmethyl)coumaran-2-one, m.p. 165°. (VIII), CH₃Ac·CO₂Et, and NaOEt–EtOH afford Et 2-(2'-methoxy-1'-naphthyl)-3 : 4-1'' : 2''-coumarano- Δ^4 -cyclohexen-6-one-1-carboxylate, m.p. 174° (oxime, m.p. 188°). (VIII) and cyclohexanone give 1-(2'-keto-1'-cyclohexyl-2''-methoxy-1''-naphthylmethyl)coumaran-2-one, m.p. 184°. A. T. P.

Pechmann condensation of p-orsellinic acid with ethyl acetoacetate. Synthesis of 7-hydroxy-4 : 5-dimethylcoumarin. S. M. SETHNA and R. C. SHAH (J. Indian Chem. Soc., 1940, 17, 211–214).—p-Orsellinic acid with CH₃Ac·CO₂Et and conc. H₂SO₄ yields, at 100°, 5-hydroxy-4 : 7-dimethylcoumarin, and at 60–70°, an 8-carboxylic acid, m.p. 225° (efferv.), which when heated gives 7-hydroxy-4 : 5-dimethylcoumarin (I), m.p. 248–250° (Ac, m.p. 119–121°, and Bz derivative, m.p. 130–131°; Me ether, m.p. 117–119°; does not give a CHPh·CH·CO₂H derivative), hydrolysed (aq. NaOH) to oracetophenone. The Me₂ ether of the latter condenses (Na) with EtOAc giving 2 : 4-dimethoxy-6-methylbenzoylacetyl methane, m.p. 74–76° (Cu derivative, m.p. 198–200°), cyclised (Ac₂O–HBr at room temp.) to the Me ether, m.p. 150–152° (unaffected by boiling with 50% EtOH–KOH), of 7-hydroxy-2 : 5-dimethylchromone, m.p. 253–255° (Ac derivative, m.p. 195–197°), differing from (I). A. Li.

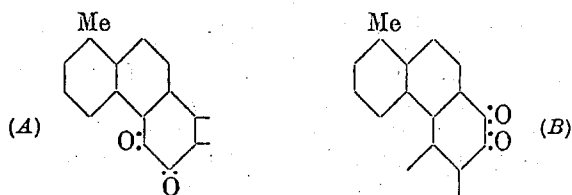
Kostanecki-Robinson reaction. I. Acetylation of oracetophenone and its monomethyl ether. S. M. SETHNA and R. C. SHAH (J. Indian Chem. Soc., 1940, 17, 239–243).—Oracetophenone

(I) with NaOAc in Ac_2O yields 7-acetoxy-, m.p. 125—126° (2:4-dinitrophenylhydrazone, m.p. 238—239°), hydrolysed by cold conc. H_2SO_4 to 7-hydroxy-5-methyl-4-acetomethylcoumarin, m.p. 214° {2:4-dinitrophenylhydrazone, m.p. 250—260° (decomp.)}; *Me ether* [also prepared from the Me_1 ether of (I), NaOAc, and Ac_2O], m.p. 123—124°, further hydrolysed by cold dil. NaOH to 7-hydroxy-4:5-dimethylcoumarin [identical with that prepared from *p*-orsellinic acid (preceding abstract)]. With NaOAc and Ac_2O this gives only the *O*-Ac derivative. The mechanism of the first reaction is discussed. A. LI.

Constituents of red sandalwood. I. Constitution of homopterocarpin. E. SPÄTH and J. SCHLÄGER (Ber., 1940, 73, [B], 1—12).—Homopterocarpin (I) (cf. Raudnitz *et al.*, A., 1935, 1372) (prep. from red sandalwood improved by removal of colouring matters from Et_2O extract with 1% KOH) is identified as 4:2'-oxido-7:4'-dimethoxyisoflavan. (I) is not recovered after dissolution in conc. H_2SO_4 ; when distilled with Pd or Se it gives no recognisable products. In AcOH with Pd- H_2 at 50—60° it gives 1-dihydrohomopterocarpin (2'-hydroxy-7:4'-dimethoxyisoflavan) (II), new m.p. 156—157°, with opening of the $\cdot\text{O}\cdot$ bridge. Alkali fusion of (II) gives $m\text{-C}_6\text{H}_4(\text{OH})_2$. (II) is sol. in dil. alkali, and with Me_2SO_4 it gives 7:2':4'-trimethoxyisoflavan (III), m.p. 61—62°, b.p. 170—180° (bath)/0.01 mm. The conclusion of Leonhardt *et al.* (A., 1936, 81) that (I) contains a CO group is incorrect; their dinitrophenylhydrazone is obtained from (II) only after long heating and (presumably) oxidation. (II) is resistant to Na-EtOH or Zn-HCl reduction, and with MgMeI gives no carbinol. PCl_5 gives only an amorphous product. With 0.5% hot aq. KOH, followed by KMnO_4 and CH_2N_2 , (II) gives the Me_2 ester of 2:5:1- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (Perkin *et al.*, J.C.S., 1908, 93, 504), also obtained from 2:5:1- $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{ONa}$ and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Me}$ at 170°, followed by hydrolysis. With hot aq. KMnO_4 , (III) gives 2:4:1-($\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$. Synthetically, 2:4:1-($\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CN}$ with $m\text{-C}_6\text{H}_4(\text{OH})_2$ and ZnCl_2 in Et_2O , followed by saturation with HCl and boiling, gives 2:4-dihydroxyphenyl 2':4'-dimethoxybenzyl ketone, m.p. 155—156°, b.p. 200—210° (bath)/0.02 mm., which with CH_2N_2 gives the corresponding 2-hydroxy-4-methoxyphenyl compound, m.p. 114—115°. This with HCO_2Et and Na at 20°, followed by ice and HCl, gives 7:2':4'-trimethoxyisoflavone, m.p. 148—149°, b.p. 190—200° (bath)/0.02 mm., reduced (Pd-C- H_2) to dl-7:2':4'-trimethoxyisoflavan (IV), m.p. 88—89°, b.p. 170—180° (bath)/0.01 mm. The difference in m.p. between (III) and (IV) is ascribed to the optical activity of (III), (IV) being racemic. (III) is not racemised at 240° in vac. (24 hr.), but either (III) or (IV) with $\text{AcOH}\cdot\text{CrO}_3$ gives 7:2':4'-trimethoxy-2:3-dihydroisoflavone, m.p. 111—112°, b.p. 180—210°/0.02 mm., converted (H_2 -Pd-C) into (IV). Possible alternative formulæ for (I) and (II) are rejected. Presence of an $\cdot\text{O}\cdot$ bridge in (I) shows that (II) cannot be a 4'-OH-compound. The bridge in (I) cannot be in the 2:2'-position, as this would imply acetal properties; a 3:2'-bridge would involve a 4-membered ring. E. W. W.

Flavans. J. B. NIEDERL and A. ZIERING (J. Amer. Chem. Soc., 1940, 62, 1157—1158).— $m\text{-C}_6\text{H}_4\text{Et}\cdot\text{OH}$ (I), cyclohexanone, and HCl (no solvent; cf. A., 1939, II, 416), first at 50° and then at room temp., or 2-cyclohexylidenecyclohexanone, (I), and HCl at room temp. give 2-2'-hydroxy-4'-ethylphenyl-7-ethyl-2:3-tetramethylene-4:4-pentamethylene-flavan, m.p. 195—196° (Br_2 -derivative, m.p. 180—181°; benzoate, m.p. 169—170°; 3:5-dinitrobenzoate, m.p. 176°; acetate, m.p. 118—119°). R. S. C.

New type of natural quinone colouring matter of the phenanthrofurans class. F. VON WESSELY and S. WANG (Ber., 1940, 73, [B], 19—24).—Tanshinone I (I) (cf. Nakao *et al.*, A., 1935, 754), new m.p. 232—234°, with Ac_2O -NaOAc-Zn gives a reduced and acetylated compound, $\text{C}_{22}\text{H}_{18}\text{O}_5$, m.p. 209° (sinters 207°). With Zn-NaOH under N_2 , followed by Me_2SO_4 , (I) in EtOH yields a reduced Me_2 ether, $\text{C}_{20}\text{H}_{18}\text{O}_3$, m.p. 93—94.5°. The quinoxaline from (I) (cf. *loc. cit.*) has new m.p. 221—222° (from Et_2O), or 196° (from melt) (dimorphous). With $\text{AcOH}\cdot\text{CrO}_3$ and some H_2SO_4 , (I) gives the anhydride (II), m.p. 196° (sinters 194°), of 1:5:6- $\text{C}_{10}\text{H}_5\text{Me}(\text{CO}_2\text{H})_2$ (III), m.p. 192° (decomp.) (cf. *loc. cit.*), which when heated with NaHCO_3 is decarboxylated to 1- $\text{C}_{10}\text{H}_7\text{Me}$. (III) very easily gives (II), which is synthesised as follows. $o\text{-C}_6\text{H}_4\text{Me}\cdot[\text{CH}_2]_2\text{Cl}$ with $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives the Et_2 ester, b.p. 185—187°/9 mm., of α -carboxy- γ -o-tolyl-*n*-butyric acid, m.p. 139° (sinters 136°), which at 160° yields γ -o-tolyl-*n*-butyric acid, m.p. 70.5° (sinters 67°), b.p. 140° (bath)/10 mm., of which the *Et* ester, b.p. 140—150° (bath)/9 mm., with KOEt and $\text{Et}_2\text{C}_2\text{O}_4$ gives *Et* α -oxalyl- γ -o-tolyl-*n*-butyric acid (decomp. on distillation at reduced pressure). This (crude) with conc. H_2SO_4 gives 1-methyl-7:8-dihydronaphthalene-



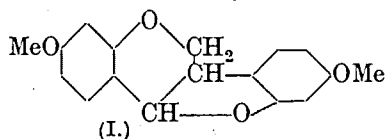
5:6-dicarboxylic anhydride, m.p. 161° (sinters 159°), dehydrogenated by S at 150—170° to (II). This (from either source) gives an ethylimide, m.p. 181.5° (sinters 178°). (I) is regarded as the *o*-quinone of a phenanthrofurans, in which (A) or (B) is linked to the residue $\cdot\text{O}\cdot\text{CH}\cdot\text{CMe}\cdot$ or $\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot$. E. W. W.

Synthetic experiments in the benzpyrone series. II. Synthesis and derivatives of flavonoid and coumarino-7':8'-5:4-furan-3-ones. L. R. ROW and T. R. SESHADRI (Proc. Indian Acad. Sci., 1940, 11, A, 206—211; cf. A., 1939, II, 278).—7-Chloroacetoxy-4-methylcoumarin (prep. by $\text{CH}_2\text{Cl}\cdot\text{COCl}$ from the 7-OH-compound at 120° or, less well, from 4-methylumbelliferone in $\text{C}_5\text{H}_5\text{N}$), m.p. 181—182°, and AlCl_3 at 175° give 4-methylcoumarino-7':8'-5:4-furan-3-one (30%), m.p. 254—256° (CHPh , m.p. 194—196°, and *Ac* derivatives, m.p. 172—173°). 7-Chloroacetoxyumbelliferone (similarly prepared), m.p. 163—164°, and AlCl_3 at 160° give coumarino-7':8'-5:4-furan-3-one, m.p. 252—253° (CHPh , m.p. 284—286°, and *Ac* derivative, m.p. 152—

153°). Similarly are prepared 7-chloroacetoxy-flavone, m.p. 138—139°, and -3-methoxyflavone, m.p. 169°, flavono-, +0.5H₂O, m.p. 206—207° (CHPh₃, +2H₂O, m.p. 224—225°, and Ac derivative, m.p. 260—261°), and 3'-hydroxyflavono-7':8':5:4-furan-3-one, +H₂O, m.p. 284—286° (CHPh₃, m.p. 274°, and Ac derivative, m.p. 192°).

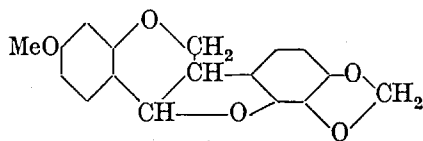
R. S. C.

Chemistry of the "insoluble red" woods. I. Pterocarpin and homopterocarpin. A. McGOOKIN, A. ROBERTSON, and W. B. WHALLEY (J.C.S., 1940, 787—795).—Homopterocarpin (I), m.p. 87°, $[\alpha]_D^{20.5}$ —236.6° in CHCl₃, contains two OMe and no OH or CO. It is oxidised (KMnO₄-COMe₂-H₂O) to 5-methoxy-2-carboxyphenoxycetic acid and 2-hydroxy-4-methoxybenzoic acid. With Pd-C-H₂ or Zn-Hg-HCl, (I) affords l-dihydrohomopterocarpin, oxidised (KMnO₄-COMe₂-H₂O) to 7-methoxychroman-3-carboxylic acid (II), m.p. 149°. O-Methyldihydrohomopterocarpin is oxidised (KMnO₄-COMe₂-H₂O) to a ketone, C₁₅H₉O₃(OMe)₃, probably an isoflavanone, m.p. 127° (2:4-dinitrophenylhydrazones, m.p. 184°; oxime, m.p. 185.5°), which is further oxidised (KMnO₄-NaOH) to a product, C₁₅H₉O₃(OMe)₃, m.p. 178°. The constitution (I) is suggested. Pterocarpin (III), m.p.



(I.)

164.5°, $[\alpha]_D^{20.5}$ —207.5° in CHCl₃, is similarly oxidised to the products obtained from (I), together with a neutral substance, m.p. 272°. Oxidation of dihydropterocarpin gives (II) but with CrO₃ a substance [2:4-dinitrophenylhydrazones, m.p. 202—203° (decomp.)] is obtained. O-Methyldihydropterocarpin is oxidised to a ketone, C₁₆H₁₀O₄(OMe)₂, m.p. 118—119° (2:4-dinitrophenylhydrazones, m.p. 248°).



(III.)

The constitution (III) is suggested. 4-O-Methyl-β-resorcyraldehyde, KOH, and Cl·[CH₂]₂·CO₂H give 5-methoxy-2-formyl-p-phenoxypropionic acid, m.p. 159° [2:4-dinitrophenylhydrazones, m.p. 241.5°; semicarbazones, m.p. 218° (decomp.)], which is oxidised (KMnO₄) to the -carboxy-acid, m.p. 143°. The formyl-acid is cyclised (NaOAc-Ac₂O) to 7-methoxy-Δ³-chromen-3-carboxylic acid, m.p. 201°, hydrogenated (Pd-C) to (II). Et 2-aldehydo-5-methoxyphenoxyacetate (2:4-dinitrophenylhydrazones, m.p. 176.5°) is cyclised (NaOEt) to Et 6-methoxycoumarone-2-carboxylate, m.p. 87° [acid (IV), m.p. 206°], and 2-aldehydo-5-methoxyphenoxyacetic acid (2:4-dinitrophenylhydrazones, m.p. 273°). The acid chloride from (IV) with HCN gives the nitrile, m.p. 101°, which could not be converted into the corresponding pyruvic acid. The acid chloride with CH₂N₂ affords the diazo-ketone, m.p. 90—91° (slight decomp.), which is converted through the amide, m.p. 148°, into 6-methoxycoumarone-2-acetic acid, m.p. 104°.

F. R. S.

5-Chloro-6-methoxy-2:1-naphththioindoxyl.—See B., 1940, 517.

Glutamic acid series. C. R. HARRINGTON and R. C. G. MOGGRIDGE (J.C.S., 1940, 706—712).—The acid chloride of α-benzyl N-carbobenzoyloxyglutamate with CH₂N₂ followed by HCl gives benzyl ε-chloro-α-carbobenzoyloxyamido-δ-ketohexoate, m.p. 125°, in which the Cl could not be replaced by H. N-p-Toluenesulphonylglutamic acid, m.p. 131°, $[\alpha]_D +22^\circ$ in EtOAc, prepared from glutamic acid, p-C₆H₄Me·SO₂Cl, and 2N-NaOH, with AcCl or Ac₂O affords the mixed anhydride of AcOH and 5-keto-1-p-toluenesulphonylpyrrolidine-2-carboxylic acid, m.p. 148°, from which the latter acid (I), m.p. 130°, $[\alpha]_D -28^\circ$ in EtOAc, is obtained by heating in 70% aq. dioxan. "p-Toluenesulphonation" of 5-ketopyrrolidine-2-carboxylic acid does not give (I) and the structure is proved as follows. The chloride of (I) with CH₂N₂-HCl yields 5-keto-1-p-toluenesulphonyl-2-chloroacetylpyrrolidine, m.p. 141°, $[\alpha]_{5461} -18.5^\circ$ in dioxan, from which the Cl is removed by H₂-Pd-CaCO₃ to form the 2-acetylpyrrolidine, m.p. 135.5°, $[\alpha]_{5461} -4.5^\circ$ in dioxan (Br-derivative, 153.5°). This compound and NaOH afford α-toluenesulphonamido-δ-ketohexoic acid, m.p. 138° [Br-derivative, m.p. 148.5° (decomp.)], which reduces Fehling's solution, is reduced by Zn-Hg-HCl to p-C₆H₄Me·SO₂·NH₂, and is oxidised (NaOBr) to dl-N-p-toluenesulphonylglutamic acid, m.p. 172.5°, also obtained by synthesis from glutamic acid. α'-Chloro-α-p-toluenesulphonamidoacetone, m.p. 142°, from p-toluenesulphonyl-glycyl chloride and CH₂N₂, and ω-p-toluenesulphonamidoacetophenone, m.p. 116°, from the K salt of p-C₆H₄Me·SO₂·NH₂ and CPh·CH₂Br, both reduce Fehling's solution and are reduced to p-C₆H₄Me·SO₂·NH₂. The chloride of (I) and NH₃ give 5-keto-1-p-toluenesulphonylpyrrolidine-2-carboxylamide (II), m.p. 196°, which with NaOH affords N-p-toluenesulphonylisoglutamine (III), m.p. 158—170°. Oxidation of (II) occurs with KOH-Br with formation of CHBr₃, (III), and increasing quantities of p-C₆H₄Me·SO₂·NH₂ with increased Br. Reduction of (III) with Na in liquid NH₃ gives N-carbobenzoyloxyisoglutamine. N-p-Toluenesulphonylaspartic anhydride, m.p. 148°, prepared from the corresponding acid and AcCl, with NaOMe in MeOH affords α(?)-Me N-p-toluenesulphonylaspartate, m.p. 96°.

F. R. S.

Metal pyridine complex salts. VI. Cobaltous and nickelous dipyridine salts of fatty acids. T. L. DAVIS and A. V. LOGAN (J. Amer. Chem. Soc., 1940, 62, 1276—1279; cf. A., 1937, II, 31).—Prep., dissociation pressure from 15° (or more) to 70—88°, and d²⁵ (and thence the shrinkage on formation) of Co^{II} and Ni^{II} (C₅H₅N)₂ acetate, propionate, butyrate, isobutyrate, and valerate are recorded. The Ni compounds are the more stable. Ni compounds have max. stability at ~60°, but Co compounds are less stable at higher temp. Increase in mol. wt. decreases the stability. C₂- and C₄-compounds are more stable than C₃- or C₅-compounds. Chain-branching has little effect.

R. S. C.

Complex compounds of platinum with complex amines.—See A., 1940, I, 299.

Some β-substituted α-picolines. A. DORNOW (Ber., 1940, 73, [B], 78—80).—Et 2-methylnicotinate shaken with 25% aq. NH₃ gives 2-methylnicotinamide

(I), m.p. 158° [*picrate*, m.p. 180—181° (decomp.)]. With NaOCl in 10% KOH (water-bath), (I) gives 3-amino-2-methylpyridine, m.p. 115—116° [*picrate*, m.p. 234° (decomp.)]; Bz derivative, m.p. 114—115°, converted into 3-iodo-, m.p. 36—37° [*picrate*, m.p. 168° (decomp.)], and 3-hydroxy-2-methylpyridine (II), m.p. 167—168° [*picrate*, m.p. 204° (decomp.)]. (I) has no antipellagra activity. (II) has not the physiological activity of adermin [lacking the 4:5-(OMe)₂ groups of the latter]. E. W. W.

M.p. of nicotinic acid. R. GORDING and L. A. FLEXSER (J. Amer. Pharm. Assoc., 1940, 29, 230—231).—Slow heating (>0.5° per min.) gives 235.5—236.6° (corr.). F. O. H.

2-Alkylmercurithiolpyridine-5-carboxylic acids. Preparation and stability of their solutions. L. A. WALTER and R. J. FOSBINDER (J. Amer. Pharm. Assoc., 1940, 29, 211—213).—The following were prepared by treating the alkylmercuric chloride (Grignard prep.) with an alkali-EtOH solution of 2-thiolpyridine-5-carboxylic acid: 2-ethyl-, m.p. 250° (decomp.), 2-n-propyl-, m.p. 210° (decomp.), and 2-n-butyl-mercurithiolpyridine-5-carboxylic acid, m.p. 190° (decomp.). These acids (as Na salts at *p*_H 8.8 or 11.0) are resistant to oxidation even in presence of catalytic metals (Cu, Mn, Fe). F. O. H.

Reaction between a highly substituted bromopyridine and lithium. C. F. H. ALLEN and G. F. FRAME (J. Amer. Chem. Soc., 1940, 62, 1301).—2-Bromo-3:4:6-triphenylpyridine and Li (not Mg) in Et₂O-N₂ give a compound, unaffected by CO₂, aldehydes, or ketones, but with cold acid giving 20—25% of 2:4:5-triphenylpyridine, m.p. 112°. 4-Bromo-2:3:5-triphenylfuran does not react with Mg or Li. R. S. C.

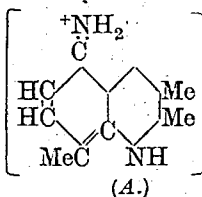
Ultra-violet absorption spectra and the formation of indole and indolenine derivatives. P. GRAMNATIKAKIS (Compt. rend., 1940, 210, 569—571; cf. A., 1939, II, 487).—The absorption spectra in EtOH of (type I) indole, *N*-ethyl- and 2:3-dimethyl-indole (I), 1:2:3:4-tetrahydrocarbazole, *N*-ethyl- and 1-methyl-1:2:3:4-tetrahydrocarbazole (II) are similar, as are those (type II) of 3:3-dimethyl-, its trimeride, and 2:3:3-trimethyl-indolenine, and 11(?) methyl-1:2:3:4-tetrahydrocarbazolenine (III). *N*:3:3-Trimethyl-2-methylene-indolenine shows marked absorption. The first band of type II is less marked and is nearer the ultra-violet than that of type I. 2-Methylcyclohexanonephenylhydrazone with MgRX or cold 2N-H₂SO₄-EtOH gives (III), b.p. 146°/12 mm., m.p. 68° (*picrate*, m.p. 170°), and (II), b.p. 185°/12 mm., m.p. 72° (*picrate*, m.p. 152°). CMePr⁸:N-NHPh similarly yields 2:3:3-trimethylindolenine and (I). *iso*Butyridenophenylhydrazone similarly gives 3-methylindole and 3:3-dimethylindolenine, b.p. 95°/12 mm., m.p. 40°. J. L. D.

Reduced isoquinolines.—See B., 1940, 495:

Synthetic drugs. I. Partial reduction of some alkyl quaternary salts of pyridine- and quinoline-carboxylamides. T. S. MA (Dissert., Chicago Univ., 1940, 1—16).—1-Propyl-1:6-dihydro-nicotinamide (cf. Karrer *et al.*, A., 1937, II, 260) with

PtO₂-H₂ in EtOH or Et₂O gives only a gummy product; neither substance has oxytocic activity. Cinchoninamide gives an *ethiodide*, m.p. 218—219°. The methiodide is reduced (Na₂S₂O₄) to a gummy product. Quinaldinamide does not react with Pr⁴I at 120—140°, but with Me₂SO₄ at 110°, followed by KI, gives its *methiodide* (I), m.p. 209—210°, also obtained by action of aq. NH₃ on Me quinaldinamide methiodide (Mills *et al.*, J.C.S., 1922, 121, 2008). Na₂S₂O₄ reduces (I) to products, m.p. 153—154°, and 225° (darkens 160°, sinters 180°), both regarded as impure 1-methyldihydroquinaldinamide, and both possessing oxytocic activity. E. W. W.

Petroleum bases. I. Reactions of 2:3:8-trimethylquinoline. A. BURGER and L. R. MODLEN, jun. (J. Amer. Chem. Soc., 1940, 62, 1079—1083).—2:3:8-Trimethylquinoline (I) and SeO₂ in boiling EtOH give 82% of 3:8-dimethylquinoline-2-aldehyde (II), m.p. 107—108° [*oxime*, m.p. 172—174° (many metallic derivatives); *semicarbazone*, sinters at 185°, m.p. 190—192° (decomp.)], which is hydrogenated (PtO₂; EtOH) to 3:8-dimethyl-2-hydroxymethylquinoline, m.p. 68—69° [*hydrochloride*, m.p. 176—185° (decomp.)]; *acetate*, m.p. 62—63°, and oxidised by Ag₂O in hot EtOH to the known acid. With CH₂N₂-MeOH, (II) gives in poor yield 3:8-dimethyl-2-quinolyl Me ketone, m.p. 90° (*oxime*, m.p. 153—154°); the corresponding *Et ketone*, m.p. 80° (*oxime*, m.p. 146—148°), is similarly but readily prepared. HNO₃ (d 1.49) converts (I) at 100° into the 5-NO₂-derivative (III), m.p. 124°, oxidised by SeO₂ to 5-nitro-3:8-dimethylquinoline-2-aldehyde, m.p. (+EtOH) 165° or (anhyd.) 167° [*oxime*, m.p. 180—181° (many metallic derivatives)], which is also obtained from (II) by boiling HNO₃ (d 1.49). SnCl₂-17% HCl at 100° reduces (III) to 5-amino-2:3:8-trimethylquinoline (IV), m.p. 110—111°, yellow (*Ac derivative*, m.p. 234—235°), which yields a red mono-(sublimes) and pale yellow *di-hydrochloride* (unstable; becomes red). The colour is due to resonance between

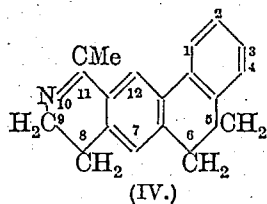


the usual *N*₁₁-hydrochloride and (A). By a diazo-reaction (IV) gives 5-hydroxy-2:3:8-trimethylquinoline, m.p. 219—219.5°, sublimes at 125°/0.1 mm. [*Me ether*, m.p. 80° (*picrate*, m.p. 198—199°); also obtained from 4:1:2-OMe-C₆H₃Me-NH₂ and tiglaldehyde]. Hydrogenation (PtO₂; AcOH) of (I) gives mixed 2:3:8-trimethyldecahydroquinoline, b.p. 89—91°/10 mm. [*hydrochloride*, m.p. 251—275° (decomp.)]. R. S. C.

Phenanthridines.—See B., 1940, 516.

Phenanthrene series. XXIV. Phenolic amino-alcohols and naphthisoquinolines derived from 9:10-dihydrophenanthrene. A. H. STUART and E. MOSETTIG (J. Amer. Chem. Soc., 1940, 62, 1110—1116; cf. A., 1939, II, 115, 343).—2-Acetoxy-7-acetyl-9:10-dihydrophenanthrene (I) and Br in Et₂O-EtOH and Hg-light give 7-bromoacetyl-, m.p. 123—124°, converted by NH₄Et-C₆H₅ into 2-acetoxy-7-β-diethylaminoacetyl-9:10-dihydrophenanthrene, m.p. 89—90°, the *perchlorate*, m.p. 165—166°, of which

with H_2 -PtO₂ in EtOH gives 2-acetoxy-, an oil (*hydrochloride*, m.p. 154—155°), hydrolysed to 2-hydroxy-7-β-diethylamino-α-hydroxyethyl-9 : 10-dihydrophenanthrene, an oil (*hydrochloride*, m.p. 202—203°). With NHEt₂ and aq. CH₂O in N₂ at 100° or NHEt₂·HCl and paraformaldehyde in boiling *iso*-C₅H₁₁·OH, (I) gives 2-acetoxy-7-β-diethylaminopropionyl- (*hydrochloride*, m.p. 132—134°) and thence 2-hydroxy-7-γ-diethylamino-α-hydroxypropyl-9 : 10-dihydrophenanthrene, m.p. (+2EtOAc) 129—130°, (solvent-free) 185—186° (*hydrochloride*, m.p. 180—181°; Bz₂ derivative *hydrochloride*, m.p. ~157—159°). 9 : 10-Dihydrophenanthrene-2-carboxylic acid (prep. from the 2-Ac derivative by 1.5% aq. NaOCl) and SOCl₂ give the acid *chloride*, m.p. 50—51°, hydrogenated (Rosenmund) to 9 : 10-dihydrophenanthrene-2-aldehyde (70%) (obtainable with difficulty directly), which with MeNO₂-NaOH-EtOH gives 2-β-nitrovinyl-9 : 10-dihydrophenanthrene, m.p. 77° (electrolytic reduction gives only 16% of amine). Me β-9 : 10-dihydro-2-phenanthrylpropionate, an oil, gives the *hydrazide*, m.p. 134—135°, and thence (Curtius) 2-β-aminoethyl-9 : 10-dihydrophenanthrene (II), an oil (*hydrochloride*, m.p. 229—230°; HCO derivative, m.p. 91°). 2-Methoxy-9 : 10-dihydrophenanthrene-7-carboxylic acid gives similarly the acid *chloride*, m.p. 87—88°, and 2-methoxy-9 : 10-dihydrophenanthrene-7-aldehyde, m.p. 100°, and thence [piperidine-CH₂(CO₂H)₂-C₅H₅N] β-2-methoxy-9 : 10-dihydro-7-phenanthryl-acrylic, m.p. 192—193°, and (H₂-PtO₂-EtOH) -propionic acid, m.p. 177° (Me ester, m.p. 61—62°; *hydrazide*, m.p. 155—156°), and 2-methoxy-7-β-aminoethyl-9 : 10-dihydrophenanthrene (III) (*hydrochloride*, sinters from 240°, m.p. indefinite). Most attempts at ring-closure of (II) and (III) failed. The Ac derivative, m.p. 112°, of (II) with POCl₃ in boiling PhMe gives 11-methyl-



5 : 6 : 8 : 9-tetrahydronaphth[2 : 1-*g*]isoquinoline (IV), the *hydrochloride*, m.p. 230—232°, of which is hydrogenated (PtO₂; EtOH) to the 5 : 6 : 8 : 9 : 10 : 11-H₆-derivative (V) (*hydrochloride*, m.p. 239—241°). With MeI-KOH-COMe₂, (V) gives 10 : 10 : 11-trimethyl-5 : 6 : 8 : 9 : 10 : 11-hexahydronaphth[2 : 1-*g*]isoquinolinium iodide (VI), m.p. 231°, decomposed at 200° to 10 : 11-dimethyl-5 : 6 : 8 : 9 : 10 : 11-hexahydronaphth[2 : 1-*g*]isoquinoline, an oil [*hydrochloride*, m.p. 234—236°; methiodide = (VI); also obtained by hydrogenating (PtO₂; EtOH) the *methiodide*, m.p. 267—268°, of (IV)]. The Ac derivative, m.p. 125—126°, of (III) gives similarly 3-methoxy-11-methyl-5 : 6 : 8 : 9-tetra- (28%) (*hydrochloride*, m.p. 249—250°; *methiodide*, m.p. 287—288°), 3-methoxy-11-methyl-5 : 6 : 8 : 9 : 10 : 11-hexa- (*hydrochloride*, m.p. 261—263°; *methiodide*, m.p. 256—258°), and 3-methoxy-10 : 11-dimethyl-5 : 6 : 8 : 9 : 10 : 11-hexa-hydronaphth[2 : 1-*g*]isoquinoline, m.p. 97—98° (*hydriodide*, m.p. 236—238°; *hydrochloride*, m.p. 200—202°). Alternative structures are possible for the tetracyclic bases. R. S. C.

Phenanthrene series. XXV. Dibenzo-[f, h]-quinoline and 7-methoxydibenzo-[f, h]quinoline.

J. KRUEGER and E. MOSSETTIG (J. Org. Chem., 1940, 5, 313—317; cf. A., 1939, II, 86).—9-Acetylphenanthrene is treated with NH₂OH·HCl in C₅H₅N-EtOH followed by HCl in boiling Ac₂O-AcOH; the product is hydrolysed and then converted by NH₃ into 9-aminophenanthrene, m.p. 128—130°, which is transformed by PhNO₂, glycerol, and H₂SO₄ at 145° into dibenzo-[f, h]quinoline (I), m.p. 167—169° (*hydrochloride*). This is hydrogenated (PtO₂ in glacial AcOH) to 1 : 2 : 3 : 4-tetrahydrodibenzo-[f, h]quinoline (II), m.p. 117—118° (corr.) (*hydrochloride*, m.p. 245—247° after softening at 230°). MeI and KOH in aq. COMe₂ convert (II) into 1-methyl-1 : 2 : 3 : 4-tetrahydrodibenzo-[f, h]quinoline, m.p. 81—83° (corr.) [*hydrochloride*, decomp. (indef.), 230—275° (corr.) after incipient melting at ~200°]. 9-Amino-3-hydroxyphenanthrene is converted by PhNO₂, FeSO₄, glycerol, and H₂SO₄ at 145° into 7-hydroxydibenzo-[f, h]quinoline, m.p. 270—273° (vac.) (*hydrochloride*, m.p. indef.). This is reduced (H₂ at 150°/140 atm.; chromite catalyst in abs. EtOH) to 7-hydroxy-1 : 2 : 3 : 4-tetrahydrodibenzo-[f, h]quinoline, m.p. 230—232° (corr.) (*hydrochloride*, m.p. 279—281°), which with MeI and KOH in aq. COMe₂ at 100° gives 7-methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydrodibenzo-[f, h]quinoline, m.p. 131.5—133° (corr.) [*hydrochloride*, m.p. 204—206° (corr.; decomp.); *methiodide*, m.p. (indef.) 200° after softening at 145° and evolving gas at 175°]. H. W.

Benz-acridones and -thioxanthenes.—See B., 1940, 433.

5 : 5-Disubstituted hydantoins. D. MARSH and C. L. LAZZELL (J. Amer. Chem. Soc., 1940, 62, 1306).—Bucherer's method gives 3—4% of 5-cyclohexyl-5-methyl-, m.p. 204—205°, 5-styryl-5-methyl-, m.p. 217° (decomp.), 5-methyl-5-β-methylpropenyl-, m.p. 209—210°, 5-p-aminophenyl-5-methyl-, m.p. 100—101°, 5-methyl-5-β-hydroxyisobutyl-, m.p. 180—181°, and 5 : 5-di-p-dimethylaminophenyl-, m.p. 136—137°, -hydantoin. R. S. C.

[Condensation products of 2-thiohydantoin.]—See A., 1940, I, 300.

1-Phenyl-3-methyl-5-pyrazolone-4-aldehyde. G. Losco (Gazzetta, 1940, 70, 284—286; cf. A., 1940, II, 55).—1-Phenyl-3-methyl-5-pyrazolone (II) and its 4-aldehyde (II) in boiling EtOH give methenylbis-4-(1-phenyl-3-methyl-5-pyrazolone) (III), which with boiling 5% NaOH regenerates (I) and (II). With KOH-EtOH-CHCl₃, (I) gives (II) and (III).

E. W. W.

Synthesis of monoketopiperazines. S. R. ASPINALL (J. Amer. Chem. Soc., 1940, 62, 1202—1204).—Gradual addition of CH₂Cl·CO₂Et, CH₂Br·CO₂Et, or CMe₂Br·CO₂Et to an excess of (CH₂·NH₂)₂ in EtOH gives 2-keto-, m.p. 136° (PhSO₂, m.p. 188°, phenylcarbamido-, m.p. 171°, and phenylthiocarbamido-derivative, m.p. 199°; *picrate*, m.p. 180°; *hydrochloride*, m.p. 208°), 2-keto-3-ethyl-, m.p. 60° (PhSO₂ derivative, m.p. 148°), and 2-keto-3 : 3-dimethyl-, m.p. 134° (PhSO₂ derivative, m.p. 206°), -piperazine, respectively. M.p. are corr. R. S. C.

Substituted vinylbarbituric acids. IV. Derivatives containing a primary Δ^1 -alkenyl group. A. C. COPE, W. H. HARTUNG, (MISS) E. M. HANCOCK, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1940, 62, 1199—1201; cf. A., 1939, II, 284).—CHR:CH·CR'(CO₂Et)₂ and CO(NH₂)₂ with NaOEt·EtOH give 12—70% of 5-ethyl-5-isobutenyl-, m.p. 161.5—162°, -n-pentenyl-, m.p. 96.5—98°, and -isopentenyl-barbituric acid, m.p. 126.5—127°, 5-n-propyl-5- Δ^1 -n-propenyl-, m.p. 150.5—151°, and -isopentenyl-barbituric acid, m.p. 101—102°, 5-isopropyl-5- Δ^1 -n-propenyl-, m.p. 140—141°, -n-pentenyl-, m.p. 94—95°, and -isopentenyl-barbituric acid, m.p. 121.5—122°, 5-n-butyl-5- Δ^1 -propenyl-, m.p. 127.5—128.5°, 2-thio-5-ethyl-5- Δ^1 - α -methyl-n-butenyl-, m.p. 150—152°, and 1-methyl-5-n-propyl-5- Δ^1 - α -methyl-n-butenyl-barbituric acid, m.p. 50.5—52.5°, 5-ethyl- (I), m.p. 109—110°, 5-n-, m.p. 83—84°, and 5-iso-propyl- (II), m.p. 107—108°, 5-n-butyl-, m.p. 111—112°, 1-methyl-5-isopropyl-, an oil, and 2-thio-5-isopropyl-, m.p. 109—110°, -5- Δ^1 -n-butenylbarbituric acid. Much alcoholysis also occurs. Structures are proved by hydrogenation of (I) and (II) and by ozonisation. β -isoPropyl- Δ^8 -hexenoamide, m.p. 123—124°, is also obtained. The acids produce powerful but very fleeting narcosis. R. S. C.

Thiobarbiturates. III. N-Substituted derivatives. F. S. CROSSLEY, E. MILLER, W. H. HARTUNG, and M. L. MOORE (J. Org. Chem., 1940, 5, 238—243; cf. A., 1936, 1125).—CEt₂(CO₂Et)₂, allylthiocarbamide, and NaOEt (mol. ratio, 1:1.6:3) condense smoothly to 5:5-diethyl-1-allyl-2-thiobarbituric acid, m.p. 97.5—98°; 5-ethyl-1-allyl-5-isoamyl-2-thiobarbituric acid, b.p. 175—180°/1 mm., is obtained similarly. With methyl-, ethyl-, or phenyl-thiocarbamide under these conditions the main products appear to be dialkyl-N-methylthiocarbamylmalonic acids of which the Me Pr^a, m.p. 109—109.5° (decomp.), Et₂, m.p. 132.5—133°, Et Pr^a, m.p. 120.5—121° (decomp.), phenylethyl-, m.p. 131—132° (decomp.), and Pr^a allyl-, m.p. 97—98° (decomp.), derivatives are described. If the mol. reactant ratio is altered to 1:1:1:1 the following -2-thiobarbituric acids are obtained: 1:5-dimethyl-5-isopropyl-, m.p. 107—107.5°; 1:5-dimethyl-5- α -methylbutyl-, b.p. 148—150°/1 mm.; 1:5-dimethyl-5- Δ^1 -cyclohexenyl-, m.p. 140—141°; 1-methyl-5:5-diethyl-, m.p. 123—124°; 1-methyl-5-ethyl-5-n-propyl-, m.p. 79—80°; 1-methyl-5-ethyl-5-isopropyl-, m.p. 104—104.5°; 1-methyl-5-ethyl-5-iso-propenyl-, m.p. 94.5—95°; 1-methyl-5-ethyl-5-isoamyl-, m.p. 84.5—85°; 5-phenyl-1-methyl-5-ethyl-, m.p. 120—121°; 5-benzyl-1-methyl-5-ethyl-, m.p. 119—119.5°; 5-benzyl-1:5-diethyl-, b.p. 170—175°/1 mm. Phenylethylacetylmethylthiocarbamide has m.p. 107—107.5°.

H. W.

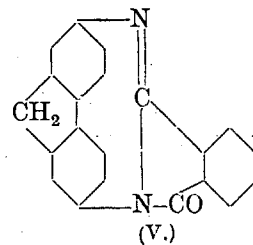
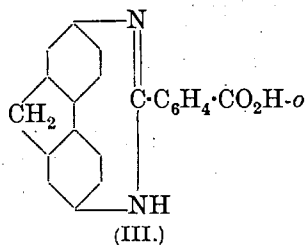
Synthetic drugs. II. Attempted synthesis of 4-methyl-5:5-dialkyluracils. T. S. MA (Dissert., Chicago Univ., 1940, 17—31).—CEt₂Ac·CO₂Et (I) does not condense with CO(NH₂)₂ or its analogues at 150—180°. With CS(NH₂)₂ and NaOEt at 120°, (I) gives a product, m.p. 210—211°. CMe₂Ac·CO₂Et, which does not react with CO(NH₂)₂, with NH₂·C(NH)·OEt at room temp. gives a product, m.p. 295° (decomp.), or at 50° or 63—65°, products, m.p. <300°. These products have high N content and

are not uracils. With large excess of SOCl₂, (I) gives a partly chlorinated product. NH:CMc·CHEt·CN with Na followed by EtI gives β -amino- α -diethylbutyronitrile (impure?), b.p. 118—120°/1 mm., which with PhNCO gives at room temp. (60 days) a very small yield of β -phenylcarbamido- α -diethyl- (impure), m.p. 233—234°, with - α -ethyl-butyronitrile, m.p. 144—145°. E. W. W.

Synthesis of pyrimidines and uric acids from cystamine. E. J. MILLS, jun. and M. T. BOGERT (J. Amer. Chem. Soc., 1940, 62, 1173—1180).—(CH₂)₂NH (which is caustic) and H₂S in much EtOH give SH·[CH₂]₂·NH₂ (I), m.p. 97—98.5° (hydrochloride, m.p. 70.2—70.7°, obtained also from 2-thiolthiazoline), but in conc. solution give (NH₂·[CH₂]₂)₂S, an oil, converted by NH₂·CO·NH·NO₂ (I) in H₂O at 100° into di- β -carbamidoethyl sulphide, m.p. 221—222°. O₂ converts (I) in H₂O or 95% EtOH into cystamine (dihydrochloride, sinters at ~206°, m.p. 212—212.5°), which with (II) gives di- β -carbamidoethyl disulphide (III), m.p. 166—167°. With CH₂(CO₂H)₂ in AcOH·Ac₂O at 65—70°, rising to 80—90°, (III) gives $\beta\beta'$ -di(carboxyacetylcarbamidoethyl) disulphide, (S·[CH₂]₂·NH·CO·NH·CO·CH₂·CO₂H)₂ (IV) (25—30%), m.p. 141—142° (gas), and a little di- β -l-barbiturylethyl disulphide (V), m.p. 216.8—218.8°. At the m.p. (IV) gives CO₂ and β -acetylcarbamidoethyl β' -carboxyacetylcarbamidoethyl disulphide, m.p. 197.5—199° (corr.), which in boiling H₂O gives di- β -acetylcarbamidoethyl disulphide, sinters at 206°, m.p. 209—210° [obtained also from (IV) by Ac₂O and a little H₂SO₄ at 100°]. With CH₂(CO₂H)₂ in Ac₂O (slight excess) at 70°, (III) gives the 3-Ac₂ derivative, sinters at 214—217°, m.p. 219—223°, of (V), hydrolysed to (V) by boiling conc. HCl. (V) is also obtained from (IV) by Ac₂O·AcOH at 80°. With NaNO₂, first in boiling H₂O and then in dil. H₂SO₄ or, better, iso-C₅H₁₁·O·NO·HCl·EtOH, (V) gives di- β -l-violurylethyl disulphide, m.p. 218.5—219.5° (decomp. from ~200°), reduced by SnCl₂·HCl at 100° to di- β -l-uramylethyl disulphide, m.p. indefinite (decomp.), which with (II) in faintly alkaline solution at 100° gives Et₂ disulphide $\beta\beta'$ -di-l-(or 3-)-uric acid, (S·[CH₂]₂·C₅H₃O₃N₂)₂, m.p. >350°. M.p. are corr. R. S. C.

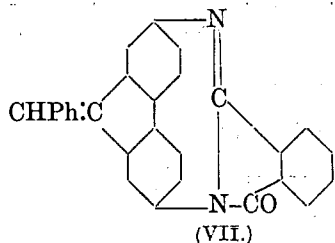
Bisisoindolenylidenes.—See B., 1940, 434.

Fluorene. I. Condensation of 2:7-diaminofluorene with phthalic anhydride. B. A. PORAI-KOSCHITZ and A. M. EFROS (Bull. Acad. Sci. U.R.S.S., 1938, Cl. Sci. Tech., No. 3, 43—60).—2:7-Diaminofluorene (I) and o-C₆H₄(CO)₂O (II) in H₂O (8 hr. at the b.p.) yield a substance said to be (III), m.p. 280°



(decomp.), together with 2:7-diphthalimidofluorene (IV), m.p. 292°. (III) is converted into the substance

(V), m.p. 340°, by heating in Ac_2O or $\text{C}_5\text{H}_5\text{N}$ (at the b.p.), or by heating alone at 120°; (V) is also prepared from (I) and (II) in NPhMe_2 at the b.p. 2-Amino-fluorene and (II) in NPhMe_2 (2.5 hr. at the b.p.) yield 2-phthalimidofluorene, m.p. 276°, the 7-*NO*₂-derivative, m.p. 308°, of which is reduced (Zn in $\text{EtOH}-\text{CaCl}_2$) to 7-amino-2-phthalimidofluorene (VI), m.p. 262°, from which (V) is obtained by boiling for 5 hr. with NPhMe_2 . (VI) and PhCHO (25 min. at the b.p.) yield 2-benzylideneamino-7-phthalimidofluorene, m.p. 246°, regenerating (VI) and PhCHO when hydrolysed (10% HCl).

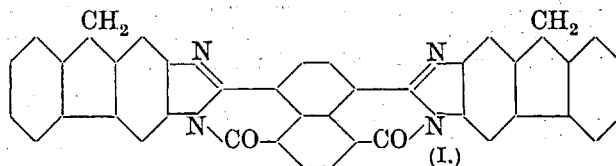


(VI) and (II) in NPhMe_2 (5 hr. at the b.p.) afford (IV), whilst in EtOH (2 hr. at the b.p.) the product is 2-phthalimido-7-fluorenylphthalamic acid. (V) and PhCHO (35 min. at the b.p.) give the substance (VII), m.p. 367°. 2-Aminofluorene and PhCHO (30 min. at the b.p.) yield 2-benzylideneaminofluorene, m.p. 152°, readily hydrolysed by acids. R. T.

1-(4'-Amino-2'-methyl-5'-pyrimidylmethyl)-2-methyl-3-β-hydroxyethylpyridinium bromide, heterovitamin-B₁. P. BAUMGARTEN and A. DORNOW (Ber., 1940, 73, [B], 44—46).—2-Methylpyridine-3-carboxylic acid hydrochloride with SOCl_2 gives the -3-carboxyl chloride hydrochloride, which with CH_2N_2 gives 3-diazoacetyl-2-methylpyridine, m.p. 58—59° (picrate, m.p. 147°), and this when heated in AcOH and treated with Zn in boiling conc. HCl yields 2-methyl-3-β-hydroxyethylpyridine (cf. Schmelkes *et al.*, A., 1939, II, 522) [methiodide, m.p. 135°; benzoate picrate, m.p. 199—200° (decomp.)], which with 4-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide in MeNO_2 at 40° gives 1-(4'-amino-2'-methyl-5'-pyrimidylmethyl)-2-methyl-3-β-hydroxyethylpyridinium bromide hydrobromide (cf. Schmelkes). This, which may be identical with Funk's S-free product (A., 1937, III, 493), has an activity 1/26 of that of vitamin-B₁. E. W. W.

Constitution of yeast ribonucleic acid. IV. Syntheses of uridylic and guanylic acids, uridine 5-phosphate, and guanosine 5-phosphate. J. M. GULLAND and G. I. HOBDAV (J.C.S., 1940, 746—752).—Phosphorylation of uridine by POCl_3 in $\text{C}_5\text{H}_5\text{N}$ gives uridine 5-phosphate, identified as the brucine salt, and with POCl_3 and Ba(OH)_2 yields a mixture of 3- and 5-phosphate, fractionated as the brucine salts; the constitutions assigned have been confirmed by comparison of the rates of liberation of free phosphate from them and from uridylic acid in hot 0.1N- H_2SO_4 . Phosphorylation of guanosine in $\text{C}_5\text{H}_5\text{N}$ with POCl_3 or PhPOCl_2 affords guanosine 5-phosphate in small yield. The 3-phosphate is obtained with Ba(OH)_2 and POCl_3 or PhPOCl_2 ; its identity with guanylic acid from yeast ribonucleic acid is proved by comparison of $[\alpha]$ and of rates of dephosphorylation in acid solution, and by a method of mixed m.p. of the brucine salts. PhPOCl_2 has been investigated as a phosphorylating agent; Ba α-glycerophosphate has been prepared. F. R. S.

Fluorene series. II. Preparation of vat diiminazole dyes of the fluorene series. B. A. PORAI-KOSCHITZ and O. K. NIKIFOROVA (J. Appl. Chem. Russ., 1940, 13, 215—221; cf. B., 1938, 40).—2:3-Diaminofluorene condenses with 1:4:5:8- $\text{C}_{10}\text{H}_4(\text{CO}_2\text{H})_4$ (12 hr. at 170—180°) giving a mixture of isomerides of (I), oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH ; 3 hr. at the b.p.) to a mixture [(I) with CO for CH_2]



of a violet and a yellow dye, or a brown dye for cotton. The H sulphate of its leuco-derivative dyes wool a bright yellow colour. R. T.

Transformation of isooxazole-3-carboxylic acids into pyrazole derivatives. IV—VI. S. CUSMANO (Gazzetta, 1940, 70, 227—235, 235—240, 240—246).—IV. 5-Phenyl- (I) and 5-methyl-isooxazole-3-carboxylic acid (II) with NHPh-NH_2 (III) and Cu in EtOH (or C_6H_6 etc.) give respectively 1:5-diphenyl- and 1-phenyl-5-methyl-pyrazole-3-carboxylic acid, which above their m.p. give the corresponding pyrazoles. If NH_2Ph is substituted for (III) there is no reaction.

V. With $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (IV) and Cu in EtOH , (I) and (II) give respectively 5-phenyl- and 5-methyl-pyrazole-3-carboxylic acid, which yield 5-phenyl- and 5-methyl-pyrazole.

VI. 5-p-Nitrophenylisooxazole-3-carboxylic acid with (III) and (IV) gives respectively 1-phenyl-5-p-nitrophenyl- (V), m.p. 255° (Et ester, m.p. 168°), and 5-p-nitrophenyl-pyrazole-3-carboxylic acid (VI), m.p. 275° (Et ester, m.p. 215°). Above the m.p., (V) gives 1-phenyl-5-p-nitrophenyl-, m.p. 93°, reduced (Zn- AcOH) to 5-p-aminophenyl-, m.p. 130° (Ac derivative, m.p. 167°), oxidised by $\text{KMnO}_4-\text{H}_2\text{SO}_4$ to 1-phenyl-pyrazole-5-carboxylic acid; (VI) gives 5-p-nitrophenylpyrazole, m.p. 195°. E. W. W.

Morpholines.—See B., 1940, 431.

Sulphathiazole. J. LAUDON and B. SJÖGREN (Svensk Kem. Tidskr., 1940, 52, 64—67).—2-Sulphanilamidothiazole (I), m.p. 200° (corr.), solubility in H_2O 0.5 g. per l. at 20° (cf. B.P. 517,272; B., 1940, 326; also Fosbinder and Walter, A., 1939, II, 525), is pharmacologically similar to the $\text{C}_5\text{H}_5\text{N}$ analogue, but is the more active against pneumococcus type V and less so against type III. M. H. M. A.

Synthesis of derivatives of 4:5'-dithiazolyl and 4:5'-glyoxalynlthiazole. E. OCHIAI, Y. TAMAMUSHI, and F. NAGASAWA (Ber., 1940, 73, [B], 28—32).— $\text{CAc}_2\text{N}\cdot\text{OH}$ with $\text{Pd}-\text{C}-\text{H}_2$ in N-HCl , followed by heating with conc. aq. KCNS , gives the 2-SH derivative (I), decomp. 308°, of 5-acetyl-4-methylglyoxaline (II), m.p. 151° (semicarbazone, m.p. 151°), into the nitrate, m.p. 200°, of which (I) is converted by boiling 10% HNO_3 . With $\text{Br}-\text{AcOH}$, (II) gives the hydrobromide, decomp. 223°, of 5-bromoacetyl-4-methylglyoxaline. This with $\text{NH}_2\cdot\text{CHS}\cdot\text{H}_2\text{O}$, $\text{CS}(\text{NH}_2)_2$, and CSMe-NH_2 in MeOH or EtOH gives respectively

4-(4'-methyl-5'-glyoxalyl)thiazole (*picrate*, m.p. 178°), and its 2-NH₂, decomp. 210° (*hydrochloride*, decomp. 253°; *acetate*, decomp. 315°), and 2-Me derivative, m.p. 183° (*hydrochloride*, m.p. 225°; *picrate*, m.p. 205°). 2-Hydroxy-5-acetyl- with Br-CHCl₃ gives 2-hydroxy-5-bromoacetyl-4-methylthiazole, m.p. 167°, which with the above reagents yields respectively 2'-hydroxy-4'-methyl-, m.p. 184.5°, 2-amino-2'-hydroxy-4'-methyl-, decomp. 225° (*hydrochloride*, m.p. 280—282°; *acetate*, decomp. above 335°), and 2'-hydroxy-2:4'-dimethyl-4:5'-dithiazolyl, m.p. 178°.

E. W. W.

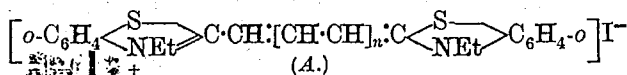
Bases of which methincyanines are the quaternary salts. (MISS) F. M. HAMER (J.C.S., 1940, 799—808).—2-Methylbenzselenzazole and *p*-C₆H₄Me·SO₃Et fused together give a substance which with 2-methylthiobenzthiazole followed by KI affords methin-[2-benzthiazole][3-(2-ethyl-dihydrobenzselenzazole)] hydriodide, m.p. 243° (decomp.), converted into the base, m.p. 134—135°. 3:3'-Diethylthiacarbocyanine iodide and NPhEt₂ yield trimethin-[2-benzthiazole][2-(3-ethyl-dihydrobenzthiazole)], m.p. 136—137°. Methin-[2-quinoline][2-(3-methyl-dihydrobenzthiazole)] forms a *hydrochloride*. 2-Methylthioquinoline and *p*-C₆H₄Me·SO₃Me give methin-[2-(1-methyl-dihydroquinoline)][2-benzthiazole], m.p. 140° [*hydriodide*, m.p. 185° (decomp.)]. Methin-[2-quinoline][2-(3-ethyl-dihydrobenzthiazole)], m.p. 151° [*hydriodide*, m.p. 264° (decomp.)], is obtained from 2-methylthioquinoline and 2-methylbenzthiazole etho-*p*-toluenesulphonate. 2-Ethylthioquinoline etho-*p*-toluenesulphonate and 2-methylbenzthiazole afford methin-[2-(1-ethyl-dihydroquinoline)][2-benzthiazole], m.p. 160° [*hydriodide*, m.p. 223° (decomp.)]. 3:1'-Dimethyl-4:5-benzthia-2'-cyanine iodide and NPhEt₂ afford methin-[2-(1-methyl-dihydroquinoline)][2-(4:5-benzbenzthiazole)], m.p. 172°; the corresponding 1-Et compound, m.p. 133°, is similarly obtained. 3:1'-Diethyl-6:7-benzthia-2'-cyanine iodide and NPhEt₂ give methin-[2-quinoline][2-(3-ethyl-dihydro-6:7-benzbenzthiazole)], m.p. 204°. Methin-[2-(1-ethyl-dihydroquinoline)][2-(6:7-benzbenzthiazole)], m.p. 228°, is obtained from 2-ethylthioquinoline etho-*p*-toluenesulphonate and 2-methyl-6:7-benzbenzthiazole. 2-Ethylthiobenzthiazole and *p*-C₆H₄Me·SO₃Et followed by KI yield methin-[4-quinoline][2-(3-ethyl-dihydrobenzthiazole)] hydriodide, m.p. 288° (decomp.), from which the base, m.p. 131°, can be obtained. 2-Ethylthioquinoline etho-*p*-toluenesulphonate and quinaldine afford methin-[2-quinoline][2-(1-ethyl-dihydroquinoline)], m.p. 140°; the corresponding 1-Me compound has m.p. 154°.

On passing from a base to the thiacyanine or selenathiacyanine which is its alkiodide, the shift of absorption max. towards the red is about the same as on passing to the corresponding acid salt. There is a greater shift on passing from trimethin base to thiacyanine (1020 Å.) or to acid salt (950 Å.). On passing from a thia-2'-cyanine base, having the alkyl-dihydro-structure in the benzthiazole nucleus, to the thia-2'-cyanine, the absorption max. shifts further towards the red (~600 Å.) than on passing to an acid salt (~450 Å.). The hitherto unknown isomeric bases with the alkyl-dihydro-structure in the quinoline nucleus have about the same absorption max. as the thia-2'-cyanines

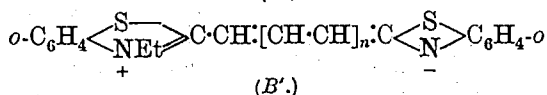
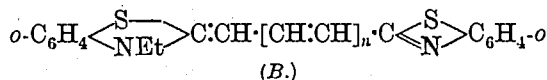
themselves; it does not shift on addition of acid but shifts towards the blue on exposure to light.

F. R. S.

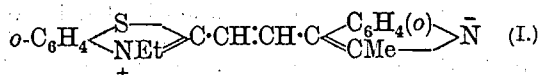
Colour and constitution. I. Halochromism of anhydronium bases related to cyanine dyes. L. G. S. BROOKER, R. H. SPRAGUE, C. P. SMYTH, and G. L. LEWIS (J. Amer. Chem. Soc., 1940, 62, 1116—1125).—Cyanine dyes (*A*; *n* = 0, 1, or 2) owe their colour to resonance; the two extreme states are identical and resonance is thus complete, leading to



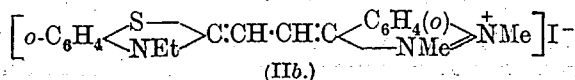
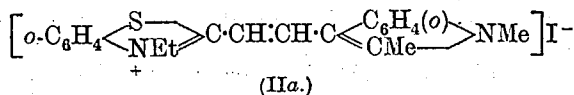
very high colour. Resonance also occurs between the forms (*B*) and (*B'*) of the corresponding bases, but the N⁻ leads to instability of (*B'*), so that the



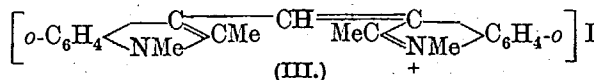
hybrid tends much more towards (*B*) and the bases are lighter in colour than the methiodides. In the mixed base, the ionic form of which is (I), the negative charge on the pyrrole N conforms to the nature of the pyrrole ring, thus stabilising (I), aiding resonance with its non-ionic form and leading to a colour which is deeper than that of (*A*). Further, the form



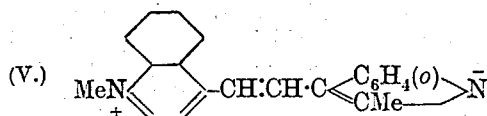
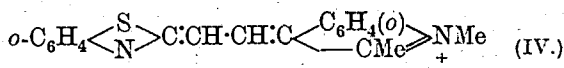
(IIa) of the methiodide of (I) is so much more favoured than (IIb) that resonance is incomplete and the colour of (II) is lighter than that of (I) (reversed halochromy). This also leads to (II) being lighter



than (*A*) or the "symmetrical" (III), the two forms of which, being identical, lead to more complete

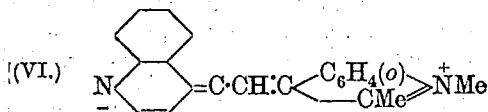


resonance. Similarly, the ionic form (IV), with the negative charge lying on the benzthiazole N, is less



stable than (I) and this base is, therefore, much less coloured. For the same reason, the base (V) is much

more deeply coloured than (VI). Dipole moments support some of the above arguments. Figures in



parentheses below are absorption max. and $\epsilon \times 10^{-4}$, unless otherwise stated in MeOH. 3:3'-Diethylthiacyanine iodide (4230 Å.; 8.45) in boiling NPhMe₂ gives the base (B; $n = 0$) (46%), m.p. 163–164° (darkens) (3960 Å.; 5.85). 2:2'-Diethylthia-carbo-cyanine iodide (5575 Å.; 14.8) and -dicarbocyanine iodide (6500 Å.; 22.9) in boiling NPhMe₂-CO₂ give 1-γ-2'-ethyl-1'-benzthiazolidene-propenyl- (65%), m.p. 138–140° (decomp.) (4580 Å.; 5.65), and -Δ^α-penta-diethyl-benzthiazole (4%), m.p. 161–162° (decomp.) (4900 Å.; 6.4). 2:2'-Diethylthiatricbocyanine has an absorption max. at 7580 Å. (24.6). 1-Methylbenzthiazole ethiodide and 2-methylindole-3-aldehyde (VII) in boiling Ac₂O give the *hydriodide* (93%), m.p. 283–284° (decomp.), whence 3-β-2'-ethyl-1'-benzthiazolidene-2-methylindolenine (I), m.p. 286–288° (5060 Å.; C₅H₅N), is obtained by NaOH-COMe₂-H₂O, which in boiling MeI-PhNO₂ gives the *methiodide* [2'-ethylbenzthiazole-1'-1:2-dimethylindole-3-dimethincyanine iodide] (II), m.p. 269–271° (decomp.) (4970 Å.; C₅H₅N), also obtained (86%) from 1-methylbenzthiazole etho-*p*-toluenesulphonate and 1:2-dimethylindole-3-aldehyde (VIII) in boiling Ac₂O (product treated with NaI). 1-Methylbenzthiazole (2 mols.) and (VIII) (1 mol.) in conc. HCl at 100° give 3-β-1'-benzthiazolylvinyl-1:2-dimethylindole (IV) (50%), m.p. 150–151° (decomp.) (3920 Å.; C₅H₅N) [ethiodide = (II)]. 1:2-Dimethylindole and (VIII) (1 mol. each) in conc. HCl give a salt, which with NaI gives *bis*-(1:2-dimethylindole-3-methincyanine iodide (III) (35%), m.p. 221–222° (decomp.) (4950 Å.; 5.3; MeNO₂). Lepidine methiodide (IX) and (VII) in boiling Ac₂O give the base (V) (72%), m.p. 249–251° (decomp.) (lit., +2CHCl₃, m.p. 240°) (5710, 6160 Å.; C₅H₅N) [*hydriodide*, m.p. 319–320° (decomp.)]. Lepidine and (VIII) in boiling HCl give 3-β-4'-quinolylvinyl-1:2-dimethylindole (VI) (43%), m.p. 192–193° (decomp.) (3940 Å.; C₅H₅N). With MeI, (V) or (VI) gives 1:2-dimethylindole-3-1'-methylquinoline-4'-dimethincyanine iodide, m.p. 297–298° (decomp.) (5390 Å.; C₅H₅N), obtained also from (IX) and (VIII) in boiling Ac₂O. R. S. C.

Cyanine dyes.—See B., 1940, 568.

Lupin alkaloids. XIX. Synthesis of racemic lupinine. K. WINTERFELD and H. VON COSEL (Arch. Pharm., 1940, 278, 70–81).—Picolinic acid is converted by short, successive treatments with SOCl₂ at 60° into the chloride, transformed by CH₂N₂ in C₆H₆ into 2-pyridyl diazomethyl ketone (*aurichloride*, m.p. 118–120°; *phenylhydrazone*, m.p. 220°), which slowly decomposes on exposure to air. It is converted by 50% AcOH at 60–70° into 2-pyridyl CH₂OH ketone (I), decomp. 160° [*aurichloride* (+1H₂O), m.p. 161°; *platinichloride*, m.p. 214–215° (decomp.); *reineckate*, decomp. 180–185°; *p-nitrophenylhydrazones*, m.p. 208–210°], which is resistant to acetylation. (I) is transformed by activated Mg and

OEt[CH₂]₃Br in Et₂O into 2-pyridylhydroxymethyl-γ-ethoxypropylcarbinol (*reineckate*, decomp. 205°), which gives OH[CH₂]₃OEt when heated at 35–45°/0.01 mm. and is hydrogenated (PtO₂ in AcOH) to 2-piperidylhydroxymethyl-γ-ethoxypropylcarbinol. This is hydrolysed and cyclised by HI (*d* 1.7) (2-α-di-iodobutylpiperidine) to *r*-lupinine, analysed as the *picro-lonate*, m.p. 179° (decomp.). H. W.

isoLobinine, a new alkaloid from *Lobelia inflata*. O. THOMÄ (Annalen, 1939, 540, 99–103).—Fraction T64 of Richter (A., 1939, III, 931) is now termed *isobobinine* (I), C₁₈H₂₅O₂N, m.p. 78° [*hydrochloride* (+H₂O), m.p. 132° (anhyd.) 154°, [α]_D²⁰ –76° in H₂O; unstable phosphate, m.p. 80°; *oxime*, an oil (*hydrochloride*, m.p. 186°)]. Catalytic reduction of (I) gives a H₂-derivative (II), b.p. 175°/4 mm., whilst thermal decomp. at 170–215°/10 mm. affords ?COMeEt (*p*-nitrophenylhydrazones, m.p. 180°). Oxidation (CrO₃) of (I) yields BzOH and AcOH; (II) gives BzOH and scopolic acid. CH. ABS. (b)

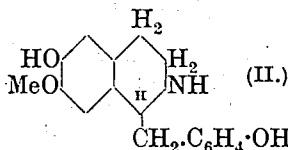
***Lobelia* alkaloids. VII. Accessory alkaloids of *Lobelia inflata*.** H. WIELAND, W. KOSCHARA, E. DANE, J. RENZ, W. SCHWARZE, and W. LINDE (Annalen, 1939, 540, 103–156; cf. A., 1932, 68).—Methods of fractionation are described. *dl*-Lelobanidine (I), C₁₈H₂₉O₂N, m.p. 68° (*hydrochloride*, m.p. 78–79°; *hydriodide*, m.p. 159°; *platinichloride*; *methiodide*, m.p. 162–164°), contains 2 OH since it gives a Bz₂ derivative, m.p. 178°. Oxidation (CrO₃, AcOH) of (I) affords *dl*-lelobanine (II), C₁₈H₂₅O₂N, oil (*perchlorate*, m.p. 136°; *hydrochloride*, m.p. 142°), oxidised (CrO₃, H₂SO₄) to AcOH, EtCO₂H, BzOH, and scopolic and methylgranatic acid (III). Successive treatment of (II) with MeI and Ag₂O (NHMe₂ evolved) gives a neutral oil, which is catalytically reduced to a glycol, C₁₇H₂₈O₂, b.p. 117–118°/0.03 mm., m.p. ~8°; this with CrO₃-dil. H₂SO₄ affords α-diketo-α-phenylundecane (IV), m.p. 51° [*semicarbazone*, m.p. 186° (decomp.)]. CO₂Et[CH₂]₇COCl, b.p. 168–169°/20 mm. (prep. by partial hydrolysis of the Et₂ ester and subsequent treatment with SOCl₂), and ZnEtI give 65% of the Et ester, b.p. 186°/21 mm., of 9-ketoundecic acid, m.p. 56° [chloride and C₆H₅ yield (IV)]. Resolution of (I) can be effected with *d*-camphorsulphonic acid; (I) is 2-β-hydroxy-β-phenylethyl-1-methyl-6-β-hydroxy-*n*-butylpiperidine. *l*-Lelobanidine I (V) [*hydrochloride* (+2H₂O), m.p. 86°, [α]_D –41.5° in EtOH; *hydriodide*, m.p. 171°; *perchlorate*, m.p. 176°; Ac₂ derivative *hydrochloride*, m.p. 195–196°; PhSO₂ derivative *hydrochloride*, m.p. 110–115°] is oxidised (CrO₃, AcOH, room temp./5 days) to *l*-lelobanine (VI) (*hydrochloride*, m.p. 186°, [α]_D +19.5° in EtOH) and also to AcOH, EtCO₂H, BzOH, and *l*-(III). *l*-Lelobanidine II [hydrochloride (+1.5H₂O), m.p. 102–105°, [α]_D –41.7° in EtOH; *hydriodide*, m.p. 165°] is also oxidised to (VI). *d*-Norlelobanidine, C₁₇H₂₇O₂N, m.p. 90°, [α]_D +62.8° in EtOH [*hydrochloride*, m.p. 193°; *hydrobromide*, m.p. 202°; *hydriodide*, m.p. 190°; (m-NO₂-C₆H₄-CO)₂, m.p. 212°, and PhSO₂ derivative, m.p. 150°], is methylated (*p*-C₆H₄Me-SO₃Me) to (V). Hofmann degradation of *d*-norlelobanine, m.p. 174°, [α]_D –11.5° in EtOH (as its methiodide), gives (III). Lobinine is oxidised

(CrO₃, 15% H₂SO₄) to BzOH (1 mol.) and a base, C₉H₁₃O₄N, m.p. 207—208° [unsaturated (KMnO₄); absorbs 2 H but does not afford a homogeneous product], and is reduced (H₂, PtO₂) to 25—30% of β-lelobanidine (*hydriodide*, m.p. 181°, [α]_D -39.2±0.5° in EtOH; *perchlorate*, m.p. 152°). *iso*Lobanine (VII) (Thomā, preceding abstract) similarly absorbs >4 H; after absorption of 4 H, (V), m.p. 83°, appears to be formed. Reduction of (VII) with 2% Na-Hg in AcOH gives a base (*hydrochloride*, m.p. 161°), differing from (X) (below) and lobinol. Oxidation (CrO₃, AcOH) of (VII) affords 50% of *isobobanine* (*hydrochloride*, m.p. 151°, [α]_D -11±0.3° in EtOH); the hygroscopic methiodide with NaHCO₃ yields an unsaturated diketone (VIII), m.p. 82—83°, also obtained from (VI). Lobinanidine (IX), C₁₈H₂₇O₂N, m.p. 95°, [α]_D -120° in EtOH [*hydrochloride*, m.p. 169°; *hydriodide*, m.p. 200°; PhSO₂ derivative, m.p. 125° (turbid; clears 135°)], is oxidised (CrO₃, AcOH, 70—80°) to lobanine (*perchlorate*, m.p. 130°) and also to lobinic acid. Catalytic reduction of (IX) gives 60% of α-lelobanidine (*hydriodide*, m.p. 174°, [α]_D -37° in EtOH) and degradation of lobanine methiodide affords (VIII). *iso*Lobinanidine (X) [*hydrochloride* (+2H₂O), m.p. 111°, [α]_D²⁰ -28.3° in H₂O; *hydriodide*, m.p. 164°] is reduced catalytically to (V). The following are also described: *base*, C₁₉H₂₆O₃N₂, m.p. 232° (decomp.) [*hydrochloride*, m.p. 299—300° (decomp.); *hydriodide*, m.p. 279°; *perchlorate*, m.p. 254—255°; *methiodide*, m.p. 244° (decomp.)]; *Bz*, m.p. 280° (decomp.), and *Br*-derivative, m.p. 288° (decomp.)]; *bases*, C₉H₁₉ON, b.p. 118—120°/1—2 mm., m.p. 85—87°, and C₁₄H₂₁ON, m.p. 103°, b.p. 135—137°/1—2 mm., separated by distillation; *base*, C₁₄H₂₁ON, m.p. 81° (*aurichloride*, m.p. 182°; *Bz* derivative, m.p. 118°), oxidised to a *ketone*, C₁₄H₁₉ON [*hydrochloride* (+H₂O), m.p. 109°] or to a compound, C₇H₁₃O₂N, m.p. 235°. OH·CHPh·CH₂·CO₂H, m.p. 116°, [α]_D -18.4±0.5°, was isolated.

CHNaAc·CO₂Et and (CH₂)₅Br₂ give CO₂Et·CHAc·[CH₂]₅·Br, converted by 48% HBr into γ-keto-octyl bromide, b.p. 202—203°/30 mm., which with CHNaBz·CO₂Et affords *Et* θ-keto-α-benzoyl-decoate. MeOH-KOH converts this into α-diketo-α-phenyldecane, m.p. 64.5° (*semicarbazone*, m.p. 194°). CO₂Et·[CH₂]₆·COCl, b.p. 146°/12 mm., gives CO₂Et·[CH₂]₆·COEt and thence αθ-diketo-α-phenyl-decane, m.p. 44—45°. CH. Abs. (b)

Curare alkaloids. V. Alkaloids of some *Chondrodendron* species and the origin of radix *pareiræ bravæ*. H. KING (J.C.S., 1940, 737—746).—When radix *pareiræ bravæ* yields *l*-bebeerine it comes from *C. platyphyllum* and when it yields *d*-bebeerine from *C. microphyllum*; *C. candicans* contains the *d*-compound. All these species contain bebeerine (*d*- or *l*-) and *d*-isochondrodendrine (I) in widely varying proportions. From the leaves of *C. platyphyllum*, there has been isolated *l*-chondrofoline, C₃₅H₃₆O₆N₂, m.p. ~135° (slow efferv.) [*nitrate*, m.p. 225° (decomp.)], which is phenolic and contains three OMe; on degradation by a one-stage Hofmann reaction it gives *O*-methylchondrofolinemethine methiodide, identical with inactive *O*-methylbebeerinemethine

methiodide *B*. A probable structure is assigned. From a large amount of radix *pareiræ bravæ* a new alkaloid, *d*-isococlaurine (II), m.p. 216—217° [*hydrochloride* (+H₂O), m.p. 175—176°, [α]_D²⁰₄₆₁ +23.9° in H₂O; *O*-methylisococlaurine methiodide, (+2H₂O), m.p. ~173°], isomeric with coclaurine, has been isolated; its constitution is as shown.



(I) forms a sulphate (+15H₂O), m.p. anhyd. 291—292° (efferv.), [α]_D²⁰₄₆₁ +115.6° in H₂O; a methiodide (+8H₂O), m.p. 287° (decomp.), [α]_D²⁰₄₆₁ +64.3° in H₂O; *O*-methylisochondrodendrine methiodide, m.p. 312° (decomp.), [α]_D²⁰₄₆₁ +1.5° in H₂O; and α-*O*-methylisochondrodendrinemethine hydrochloride (+2H₂O), m.p. 299° (decomp.). Probable structures are assigned to (I), and protocuridine and neoprotocuridine, isomeric phenolic alkaloids of pot-curare. A classification of certain bisbenzylisoquinoline alkaloids is given.

F. R. S.

Two-dimensional chromatography. C. LAPP and K. ERALI (Bull. Sci. pharmacol., 1940, 42, 49—58).—In a rapid micro-chromatographic method for the separation and determination of very small amounts of org. substances, these are adsorbed on a thin layer of MgO, MgCO₃, or kaolin, and after washing with an org. solvent, the layer of adsorbent is dried, and the type and degree of fluorescence in Wood's light are determined.

J. N. A.

Determination of arsenic in organic arsenic compounds. R. TIOLLAIS and H. PERDREAU (Bull. Sci. pharmacol., 1940, 42, 58—64).—The substance is boiled with conc. H₂SO₄ until decolorised and, after dilution and neutralisation with NaOH, the As₂O₃ is titrated with 0.1N-I in presence of KHCO₃. The method is rapid and accurate, and applicable to arsenicals in general if Cl is absent.

J. N. A.

Determination of glycerol. H. KA (J. Agric. Chem. Soc. Japan, 1940, 16, 461—475).—A method utilising the Lovibond Tintometer, based on Denigès' colour reaction with codeine after removal of impurities with CaO, is described.

H. G. R.

Colorimetric micro-determination of formaldehyde. D. MATSUKAWA (J. Biochem. Japan, 1939, 30, 385—394).—The sample (2 c.c. of 0.02—1.0 mg.-% solution of CH₂O) is treated with 0.5% NHPH·NH₂ at 40°, 2.5% K₃Fe(CN)₆ is added followed by conc. HCl, and the red colour that develops is evaluated in a step-photometer. The method is exemplified by change in concn. of CH₂O in toxin preps. during incubation.

F. O. H.

Detection and determination of picrolonic acid. S. FUKUDA (J. Biochem. Japan, 1939, 30, 465—471).—Picrolonic acid (I) (2 mols.) rapidly heated to 124° condenses (with liberation of NO and H₂O) to give a substance, C₂₀H₁₄O₇N₆, which with NaOH produces a deep red colour. This reaction is used for the detection and (approx.) determination of (I). With arginine, lysine, and spermidine picrolonates, the method gives vals. ~85% of those calc. for the (I) content.

F. O. H.

A., II.—Organic Chemistry

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B.p. relationships among aliphatic hydrocarbons.—See A., 1940, I, 353.

Rotation isomerism in dissolved $\alpha\beta$ -di-iodoethane.—See A., 1940, I, 346.

Isomerisation equilibrium of *n*- and *iso*-butane.—See A., I, 1940, 352.

Redistribution reaction. IX. Redistribution of halides and esters. G. CALINGAERT, H. SOROOS, V. HNIZDA, and H. SHAPIRO (J. Amer. Chem. Soc., 1940, 62, 1545—1547; cf. A., 1940, II, 300).—Random distribution is achieved by equilibrating $(\text{CH}_2\text{Cl})_2$, $(\text{CH}_2\text{Br})_2$, $\text{EtBr}-(\text{CH}_2\text{Cl})_2$, and $\text{EtCl}-(\text{CH}_2\text{Br})_2$ by 1.5—3 mol.-% of AlCl_3 ; the equilibrium mixture contains more EtCl than EtBr . Random distribution is also obtained by $\text{Al}(\text{OEt})_3$ at 100° from $\text{Me}_2\text{C}_2\text{O}_4$ — $\text{Bu}_2\text{C}_2\text{O}_4$, EtOAc — PrCO_2Me , and EtOAc —furfuryl furoate. Departure of such mixtures from equimolarity gives information concerning relative bond strengths. R. S. C.

Thermal decomposition of $\beta\beta$ -dimethyl- γ -amyl acetate. P. L. CRAMER and V. A. MILLER (J. Amer. Chem. Soc., 1940, 62, 1452—1454).— $\text{CH}_2\text{EtBu}^\gamma\text{OAc}$ (prep. from $\text{CH}_2\text{EtBu}^\gamma\text{OH}$ by AcCl), b.p. 153 — 158° , when passed over glass wool at 400° (little change at 350°), gives 90.5% of $\text{CHMe}:\text{CHBu}^\gamma$, b.p. 76.6 — 76.7° , with 7% of a $\beta\gamma$ - and $\beta\delta$ -dimethylpentene (hydrogenation led to some CHMeEtPr^β). The yield is thus $>$ by decomp. of the xanthate. R. S. C.

Behaviour of substituted allenes towards Meinel's colour test. F. B. LAForge and F. ACREE, jun. (J. Amer. Chem. Soc., 1940, 62, 1621—1622).—Meinel's test (A., 1937, II, 173) is given by $\text{CHMe}:\text{C}:\text{CHPh}$, $\text{CHMe}:\text{C}:\text{CHMe}$, α -cyclohexyl- $\Delta^{\beta\gamma}$ -pentadiene, and pyrethron, and is thus not sp. for $\text{C}:\text{C}:\text{C}:\text{C}$. The intensity of the colour and the speed of reaction with myrcene, $\text{CH}_2:\text{CHPr}^\alpha$, and $\text{CHPhBr}:\text{CH}_2\text{Br}$ decrease in the order given. R. S. C.

Substituted acetylenes and their derivatives. XL. Preparation of *tert.* acetylenes. K. N. CAMPBELL and L. T. EBY (J. Amer. Chem. Soc., 1940, 62, 1798—1800).— $\text{CEt}:\text{C}:\text{CMeEt}\cdot\text{OH}$ and gaseous HCl at $<0^\circ$ give 66% of γ -chloro- γ -methyl- Δ^{δ} -*n*-heptinene (I), b.p. $64^\circ/25$ mm., which with MgMeI gives $\gamma\gamma$ -dimethyl- Δ^{δ} -*n*-heptinene (66%), b.p. $69^\circ/100$ mm., and thence (H_2 —Raney Ni— MeOH or H_2 —PtO₂—abs. EtOH) $\text{CMe}_2\text{EtBu}^\alpha$, b.p. $135^\circ/735$ mm., obtained also (28%) from $\text{MgBu}^\alpha\text{Br}$ and CMe_2EtBr at 50 — 70° (later at the b.p.). With MgEtBr , (I) gives γ -methyl- γ -ethyl- Δ^{δ} -*n*-heptinene, b.p. $88^\circ/100$ mm., and thence $\text{CMeEt}_2\text{Bu}^\alpha$, b.p. $155^\circ/734$ mm. Similarly are prepared: (a) β -chloro- β -methyl- Δ^γ -*n*-octinene (II), b.p.

$68^\circ/15$ mm., and thence $\beta\beta$ -dimethyl- Δ^γ -*n*-octinene, b.p. $79^\circ/70$ mm., and $n\text{-C}_5\text{H}_{11}\cdot\text{CH}_2\text{Bu}^\gamma$, b.p. $62^\circ/30$ mm.; (b) γ -chloro- γ -methyl- Δ^{δ} -*n*-noninene (III), b.p. $82^\circ/17$ mm.; (c) γ -chloro- γ -methyl- Δ^{δ} -*n*-decinene, b.p. $90^\circ/10$ mm., and thence $\gamma\gamma$ -dimethyl- Δ^{δ} -*n*-decinene, b.p. $86^\circ/20$ mm., and $n\text{-C}_6\text{H}_{13}\cdot\text{CMe}_2\text{Et}$, b.p. $89^\circ/20$ mm., and (d) γ -chloro- γ -methyl- Δ^{δ} -*n*-pentinene, b.p. $55^\circ/130$ mm. $\gamma\gamma$ -Dimethyl- Δ^{δ} -*n*-noninene, b.p. $82^\circ/40$ mm., is obtained from (III) and MgMeI , (II) and MgEtI , or (3% yield) CMe_2EtBr and $\text{CBu}^\alpha:\text{C}:\text{MgCl}$, and is reduced to $n\text{-C}_5\text{H}_{11}\cdot\text{CMe}_2\text{Et}$, b.p. $84^\circ/30$ mm., obtained also (23% yield) from $n\text{-C}_6\text{H}_{13}\cdot\text{MgBr}$ and CMe_2EtBr . R. S. C.

Substituted acetylenes and their derivatives. XXXVIII. Chlorides and hydrochlorides from Δ^{α} -hexinene. G. F. HENNION and C. E. WELSH. XXXIX. Chlorination of the acetylenic alcohols derived from acetone. G. F. HENNION and G. M. WOLF (J. Amer. Chem. Soc., 1940, 62, 1367—1368, 1368—1371; cf. A., 1939, II, 400; 1940, II, 187).—XXXVIII. $\text{CH}:\text{CBu}^\alpha$ (I) (41 g.) and Cl_2 in CCl_4 containing SbCl_5 (1.5 ml.) at $45\pm5^\circ$ give *trans*- $\text{CHCl}:\text{CBu}^\alpha\text{Cl}$ (19.6%) and $\text{CHCl}_2:\text{CBu}^\alpha\text{Cl}_2$ (II) (30.6%). HCl adds to (I) in C_6H_6 , preferably in presence of BiCl_3 at 80 — 85° , giving β -chloro- Δ^{α} -*n*-hexene (III) (20%), b.p. $113^\circ/740$ mm., and $\beta\beta$ -dichloro-*n*-hexane (40%), b.p. $68^\circ/49$ mm. [converted by KOH — $\text{Pr}^\alpha\text{OH}$ at 95° into (III) (60.5%)]. Cl_2 and (III) in CCl_4 containing SbCl_5 at 35 — 40° give (II) (25.4%) and *cis*- $\text{CHCl}:\text{CBu}^\alpha\text{Cl}$ (26.7%). Physical consts. of the products are reported.

XXXIX. $\text{CH}:\text{C}:\text{CMe}_2\cdot\text{OH}$ and Cl_2 at 25 — 30° (a) in CCl_4 give *trans*- $\alpha\beta$ -dichloro- γ -methyl- Δ^{α} -*n*-buten- γ -ol (I) (22%), b.p. 64 — $66^\circ/6$ mm., and $\alpha\alpha\beta\beta$ -tetrachloro- γ -methyl-*n*-butan- γ -ol (II) (44.6%), b.p. 95 — $97^\circ/6$ mm., (b) in MeOH give (I) (20.6%), (II) (32.1%), *cis*- $\alpha\beta$ -dichloro- γ -methyl- Δ^{α} -*n*-buten- γ -ol (III) (6.9%), b.p. 76 — $78^\circ/6$ mm., and $\alpha\alpha$ -dichloro- γ -methyl-*n*-butan- γ -ol- β -one (IV) (10.5%), b.p. 58 — $60^\circ/6$ mm. [by way of $\text{OH}:\text{CMe}_2:\text{C}(\text{OMe}):\text{CHCl}$], and (c) in H_2O give (III) (15.5%) and $\alpha\gamma\gamma$ -trichloro- γ -methyl-*n*-butan- β -one (V) (30%), b.p. 61 — $63^\circ/6$ mm. [by interaction of (IV) and HCl]. In MeOH at 60 — 65° , no (III) but more (II) is formed. With aq. $\text{CaCl}:\text{OCl}$, (IV) gives CHCl_3 . KOH —aq. MeOH converts (V) exothermally into $\alpha\alpha$ -dichloro- γ -methyl- Δ^γ -*n*-buten- β -one (60%), b.p. 64 — $66^\circ/6$ mm. Chlorination of $(\text{C}:\text{CMe}_2\cdot\text{OH})_2$ is accompanied by cyclodehydration: at 60 — 65° in CCl_4 $\gamma\gamma\delta\delta$ -tetrachloro- $\beta\epsilon$ -dimethyl-*n*-hexane- $\beta\epsilon$ -diol (4.6%), b.p. 82 — $84^\circ/6$ mm., 3:4-dichloro-2:2:5:5-tetramethyl-2:5-dihydrofuran (8.6%), b.p. 46 — $48^\circ/6$ mm., and 3:3:4:4-tetrachloro-2:2:5:5-tetramethyl-tetrahydrofuran (VI) (45.8%), b.p. 96 — $98^\circ/6$ mm., are formed; in MeOH , (VI) (46.6%) with $\gamma\gamma$ -dichloro-

β -dimethyl-*n*-butan- δ -one- β -diol (VII) (1.7%), m.p. 99°, and 4:4-dichloro-3-keto-2:2:5:5-tetramethyl-tetrahydrofuran (VIII) (14.6%), b.p. 84–86°/6 mm. [both formed by way of $\text{OH}\cdot\text{CMe}_2\cdot\text{C}(\text{OMe})\cdot\text{CCl}\cdot\text{CMe}_2\cdot\text{OH}$], are produced; in H_2O , (VIII) (57.5%) and (VII) (3.2%) are obtained. *n*, *d*, $[\alpha]$, and parachors of the products are reported.

R. S. C.

Hindered rotation in $\text{CH}_3\text{D}\cdot\text{CH}_2\text{Br}$.—See A., 1940, I, 283.

Raman spectra of ethylene chlorohydrin, *n*-propyl chloride, and *n*-butane in the liquid and solid states.—See A., 1940, I, 346.

Esterification of primary alcohols without the use of acids.—See B., 1940, 512.

Linoleyl alcohol. II. Preparation, properties, and rearrangement. J. P. KASS and G. O. BURR (J. Amer. Chem. Soc., 1940, 62, 1796–1798; cf. A., 1939, II, 137).—Me linoleate and Na-EtOH give linoleyl alcohol (I), f.p. $<-16^\circ$, b.p. 153–154°/3 mm., isomerised by KOH-BuOH to a mixture of Δ^8 -octadecadienols, identical with that obtained from the ester by Na-BuOH. The tetrabromide, m.p. 87.5–88°, of (I) is oxidised (KMnO_4) to tetrabromostearic acid, m.p. 112–114°. Me linoleate and Na-EtOH give linolenyl alcohol, b.p. 133°/2 mm. (hexabromide, sinters at 171°, m.p. 172°). R. S. C.

Keten acetals. VI. Preparation of keten acetals from α -bromo-ortho-esters. P. M. WALTERS and S. M. McELVAIN (J. Amer. Chem. Soc., 1940, 62, 1482–1484; cf. A., 1940, II, 202).—66% of $\text{CH}_2\text{C}(\text{OEt})_2$ is obtained from $\text{CH}_2\text{Br}\cdot\text{C}(\text{OEt})_3$ by Na in boiling C_6H_6 , but Zn or Mg gives multimol. products. *Et*₃ α -bromo-orthopropionate, b.p. 73°/8 mm., and Na give similarly methylketen *Et*₂ acetal, b.p. 133–134°/760 mm., 77–78°/100 mm., which with H_2O or EtOH and a trace of HCl gives exothermally EtCO_2Et and $\text{CEt}(\text{OEt})_3$, respectively.

[JONES] $\text{CHBr}\cdot\text{CH}(\text{OEt})_2$ (*R* = Me, Et, or Pr^i) and $\text{CMe}_2\text{Br}\cdot\text{CH}(\text{OEt})_2$ with $\text{KO}^i\text{Bu}\cdot\text{Bu}^i\text{OH}$ suffer $\alpha\beta$ -loss of HBr. R. S. C.

Solid derivatives of monoalkyl ethers of ethylene glycol and diethylene glycol. J. P. MASON and J. F. MANNING (J. Amer. Chem. Soc., 1940, 62, 1635–1640).— $\text{ONa}\cdot[\text{CH}_2]_2\cdot\text{OMe}$ and $\text{ONa}\cdot[\text{CH}_2]_2\cdot\text{OEt}$ with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in boiling $\text{C}_5\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ give β -methoxy-, b.p. 149–149.5°/18 mm. (*p*-phenylphenacetyl ester, m.p. 68°; piperazinium salt, B_2H_X , m.p. 44.5–45°), and β -ethoxy-ethoxyacetic acid, b.p. 154.5–155° (*p*-phenylphenacetyl ester, m.p. 52.5–52.8°; piperazinium salt, B_2H_X , m.p. 87–87.5°). $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{OR}$ give the *p*-nitrobenzoates, *R* = Me, b.p. 192.5–195°/16 mm., Et (I), b.p. 197–199°/16 mm., and Bu, b.p. 208.8–211°/16 mm., reduced by, best, Fe powder and HCl to the *p*-amino-benzoates, *R* = Me, m.p. 79.7°, b.p. 217.5–219°/16 mm., Et, m.p. 79.2°, b.p. 223–224.5°/16 mm., and Bu, m.p. 36.2–36.5°, b.p. 232.5–234°/16.5 mm. (cf. A., 1935, 1494), and thence the azo-dyes, *p*- $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, *R* = Me, m.p. 108.2°, Et, m.p. 103°, and Bu, m.p. 87.8–88.4°. $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{OR}$ give similarly the *p*-nitro-, *R* = Et, b.p. 222.5–224°/16 mm., and Bu, b.p.

246–249°/16 mm., and *p*-amino-benzoates, *R* = Et, m.p. 64.4°, b.p. 257–259°/20 mm. ($\text{N}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}$: derivative, m.p. 87.8–88.4°), and Bu, b.p. 262.5–265°/16 mm. ($\text{N}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}$: derivative, m.p. 57.2°). Zn dust and NH_4Cl in 75% EtOH reduce (I) to the azo-compound, m.p. 94.8° (*loc. cit.* 97°). $\text{ONa}\cdot[\text{CH}_2]_2\cdot\text{OR}$ and β -4-morpholinoethyl chloride in boiling dioxan give 4- β - β' -methoxy-, b.p. 119–120°/8 mm. (*picrate*, m.p. 111.3°; *hydrochloride*, m.p. 97.2–97.5°), -ethoxy-, b.p. 132–133°/10 mm. (*picrate*, m.p. 111.1°; *hydrochloride*, m.p. 99.5–100.5°), and -butoxy-ethoxyethylmorpholine, b.p. 154–157°/9 mm. (*picrate*, m.p. 62–62.5°; *hydrochloride*, m.p. 59.5–60°). $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{OR}$ gives similarly 4- β - β' - β'' -ethoxy-, b.p. 163–165°/9 mm. (*picrate*, m.p. 204.8–207°; *hydrochloride*, m.p. 150–151°), and -butoxy-ethoxyethoxyethylmorpholine, b.p. 189–192°/8 mm. (*picrate*, m.p. 161–161.5°). $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{OMe}$, paraformaldehyde, and NH_4Et give β -methoxyethoxymethyl-diethylamine, b.p. 73–74.5°/16 mm. (ethiodide, m.p. 49.5°). Attempts to prepare other solid derivatives failed.

R. S. C.

Acid iodides. IV. Mechanism of ether cleavage. P. G. STEVENS (J. Amer. Chem. Soc., 1940, 62, 1801–1802; cf. A., 1933, 391).—Cleavage of ethers by RI proceeds by way of an oxonium iodide (Ingold's S_N2 reaction with inversion), since $\text{CHMeBu}^i\cdot\text{OMe}$, $\alpha_{\text{D}}^{25} + 7.63^\circ$, and $\text{CH}_2\text{Cl}\cdot\text{COI}$ at 20–25° give 28.8% of CHMeBu^iI , $\alpha_{\text{D}}^{25} - 19.42^\circ$, and 52.4% of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\cdot\text{CHMeBu}^i$, b.p. 80.0–80.3°/9 mm., $\alpha_{\text{D}}^{25} + 8.06^\circ$, with MeI, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Me}$, and a little olefine. Physical consts. are recorded. R. S. C.

Sulphur. XVI. Synthesis of higher alkyl sulphonium salts and related compounds. R. W. BOST and J. E. EVERETT (J. Amer. Chem. Soc., 1940, 62, 1752–1754; cf. A., 1940, II, 117).— RSNa and RT in EtOH give *Et* cetyl, m.p. 19°, b.p. 201–205°/12 mm. (HgCl_2 , m.p. 75.5°, and HgBr_2 additive compounds, m.p. 58°), and lauryl sulphide, m.p. -6° to -5° , b.p. 167–171°/18 mm., which with MeI, best in MeOH, give methylethyl-cetyl-, m.p. 73° (corresponding bromide, m.p. 77°, and nitrate, m.p. 61°), and lauryl-sulphonium iodide, m.p. 65°, and with KMnO_4 give *Et* cetyl, m.p. 88°, and lauryl sulphone, m.p. 78.5°.

R. S. C.

Reaction of organic halides with piperidine.

VI. Branched-chain β -bromo-esters. E. L. FOREMAN and J. M. McELVAIN (J. Amer. Chem. Soc., 1940, 62, 1438–1441).—Absence of H from C_{10} renders impossible elimination of HBr from $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ and $\text{CHMeBr}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, which with piperidine give only small amounts of *tert.* amine, thus confirming the mechanism described in Part V (A., 1940, II, 302). The chain-branching does not affect elimination of HBr but greatly reduces the amount of *tert.* amine formed, examples being *Et* β -bromoisohexanoate (I), b.p. 63–64°/0.1 mm., β -bromogamma-dimethylvalerate (II), b.p. 65–66°/0.1 mm., and 2-bromocyclohexanecarboxylate (prep. from Et hexahydrosalicylate by PBr_3 in C_6H_6), b.p. 75–76°/0.1 mm. $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ and PBr_3 in C_6H_6 at room temp. give 25% of Br-esters (A), b.p. 90–92°/20 mm., and much of the phosphite, converted by 48% HBr into (A). (A) contains much $\text{CMePr}^i\text{Br}\cdot\text{CO}_2\text{Et}$,

which is removed by interaction with piperidine (gives $\text{CMe}_2\text{:CMe}\cdot\text{CO}_2\text{Et}$), and then yields *Et* β -bromo- α -dimethyl-*n*-butyrate, b.p. 72—74°/8 mm.

$\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ and PBr_3 give $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, b.p. 62—63°/7 mm. $\text{CHPr}^{\beta}\cdot\text{C}(\text{CO}_2\text{Et})_2$ (prep. described), b.p. 117—119°/13 mm., and aq. KOH give $\text{CHPr}^{\beta}\cdot\text{C}(\text{CO}_2\text{H})_2$, which at 150°/20 mm. gives 21% of $\text{CHPr}^{\beta}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, b.p. 114—115°/18 mm., and 20.2% of isohexolactone, b.p. 96—98°/18 mm. $\text{CHPr}^{\beta}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, b.p. 171—173°, and HBr in CHCl_3 at room temp. give 86.5% of (I), which could not be obtained pure from the OH-ester. $\text{Bu}^{\gamma}\text{CHO}$ and $\text{CH}_2(\text{CO}_2\text{Et})_2$ give *Et* γ -dimethyl- Δ^{α} -pentenoate, b.p. 138—140°/23 mm., converted by hydrolysis and decarboxylation into $\text{CHBu}^{\gamma}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m.p. 62—63°, b.p. 126—131°/23 mm., which with HBr—EtOH gives (II). R. S. C.

Preparation of fatty acid β -monoglycerides. B. F. DAUBERT (J. Amer. Chem. Soc., 1940, 62, 1713—1714).— $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{O}\cdot\text{CPh}_2)_2$ and $n\text{-C}_{15}\text{H}_{31}\cdot\text{COCl}$ in quinoline— CHCl_3 at 0° give the β -palmitate, m.p. 71°, hydrogenated (Pd-black; 45—50°/3 atm.; abs. EtOH) to β -monopalmitin (85%), m.p. 68°, and CHPh (cf. Verkade *et al.*, A., 1937, II, 318). α' -Benzylideneglycerol and PrCOCl in $\text{C}_5\text{H}_5\text{N}$ at 0° give the β -butyrate, m.p. 16—18°, 165°/5 mm., and thence β -monobutylin and α' -distearin β -butyrate, m.p. 51.5° (lit. 51°). R. S. C.

Oxidative cleavage of α -keto-acids and -alcohols by means of lead tetra-acetate. E. BAER (J. Amer. Chem. Soc., 1940, 62, 1597—1606).—Acids, $\text{COR}\cdot\text{CO}_2\text{H}$, are unchanged by $\text{Pb}(\text{OAc})_4$ in AcOH, except for the effects of traces of H_2O . In presence of reagents $\text{R}'\text{H}$ ($\text{R}' = \text{OH}$, OMe , OEt , $\text{O}\cdot\text{CH}_2\text{Ph}$, CN), which by addition generate a glycol-like grouping, $\text{OH}\cdot\text{CRR}'\cdot\text{CO}\cdot\text{OH}$, rapid reduction of 1 mol. of $\text{Pb}(\text{OAc})_4$, generation of 1 mol. of CO_2 , and formation of CORR' occur. This is established for AcCO_2H in presence of MeOH and $\text{CH}_2\text{Ph}\cdot\text{OH}$ (isolation of $\text{CH}_2\text{Ph}\cdot\text{OAc}$), $\text{COBu}^{\gamma}\cdot\text{CO}_2\text{H}$ in presence of H_2O (isolation of $\text{Bu}^{\gamma}\text{CO}_2\text{H}$) or MeOH, and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (isolation of $\text{Bu}^{\gamma}\text{CO}_2\cdot\text{CH}_2\text{Ph}$), and BzCO_2H in presence of H_2O (isolation of BzOH), EtOH (isolation of EtOBz), and HCN (isolation of BzCN).

$\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ in presence of H_2O undergoes also acetylation to $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, since after hydrolysis $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (50.6%) is isolated and a second mol. of $\text{Pb}(\text{OAc})_4$ is consumed. The CO_2 liberated (95—103.2 mol.-%) and $\text{Pb}(\text{OAc})_4$ consumed (1.07—0.95 mol.-%) were determined in most cases. Enolisation plays no part in the above reactions.

α -CO-alcohols $\text{COR}\cdot\text{CHR}'\cdot\text{OH}$ are slowly oxidised to the diketones by $\text{Pb}(\text{OAc})_4$ in AcOH in absence of OH-forming substances, but in presence of such substances ($\text{R}''\text{OH}$) undergo very rapid oxidative cleavage to CORR'' and $\text{R}'\text{CO}_2\text{H}$. These reactions are verified for $\text{COMe}\cdot\text{CHMe}\cdot\text{OH}$ alone [gives Ac_2 (41.6%)] and in presence of H_2O [gives MeCHO (95%)], $\text{COPh}\cdot\text{CH}_2\cdot\text{OH}$ at 50—55° in presence of H_2O [gives BzOH (78.6%)] and EtOH [gives EtOBz and thence BzOH (60%)], benzoin alone (gives 83.4% of Bz_2) and in presence of H_2O (75% of PhCHO isolated) and EtOH (84% of EtOBz isolated),

and anisoin alone (gives 74% of anisil and 20% of $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$) and in presence of H_2O (76.8% of $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, 83% of $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and 5% of anisil isolated) and EtOH (gives $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$). R. S. C.

Acetoacetyl chloride. C. D. HURD and C. D. KELSO (J. Amer. Chem. Soc., 1940, 62, 1548—1549).—Passage of HCl into $\text{CHAc}\cdot\text{CO}$ at -7° and then cooling to -50° gives $\text{CH}_2\text{Ac}\cdot\text{COCl}$, m.p. -50° to -51°, which at $>-20^\circ$ gives HCl and dehydroacetic acid, with NH_2Ph or EtOH at -60° gives $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{NHPh}$ or $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, respectively, and with $\text{C}_6\text{H}_6\text{-AlCl}_3$ (27%) or MgPhBr (12%) at -50° gives $\text{COMe}\cdot\text{CH}_2\cdot\text{COPh}$, obtained in 10.5% yield from $\text{CHAc}\cdot\text{CO}$ by $\text{C}_6\text{H}_6\text{-AlCl}_3$. R. S. C.

Optical superposition. IX. *l*-Menthyl esters of mucic and tetrahydroxyadipic [1.2.3.4.] acids. R. W. LAPSLEY, J. ROBERTSON, and T. S. PATTERSON (J.C.S., 1940, 862—866).—Previous conclusions (A., 1927, 229) are invalidated since Posternak (A., 1936, 55) showed that Fischer's "allomucic acid" has not the structure assigned to it. The products of epimerisation ($\text{C}_5\text{H}_5\text{N}$ at 135—140°) of mucic acid with Ac_2O and a trace of H_2SO_4 yield small quantities of tetra-acetylmucic and tetra-acetoxymucic acids, also obtained in good yield from Δ -talomucic acid, Ac_2O and H_2SO_4 . Tetra-acetoxymucic acid, SOCl_2 , m.p. 165°, yields *Et*, m.p. 136°, and *l*-menthyl tetra-acetoxymucate, m.p. 135—136°, $[\alpha]_{\text{D}}^{20} +72.7^\circ$ in C_6H_6 . *l*-Menthyl tetra-acetylmucate, m.p. 153°, has $[\alpha]_{\text{D}}^{20} +50.2^\circ$ in C_6H_6 . These rotations disagree with van 't Hoff's principle of optical superposition. The following were prepared: *Et* tetra-acetyl- Δ -talomucate, m.p. 108—109°, Δ -, m.p. 102—103°, and Δ -sec-octyl tetra-acetylmucate, m.p. 114—115°; Δ -sec-octyl tetra-acetoxymucate could not be obtained sufficiently pure for comparison. $[\alpha]$ of *l*-menthyl dehydromucate (from *l*-menthol, mucic acid, and HCl at 165°) at various temp. and $\lambda\lambda$ is recorded. A. LI.

Preparation of *d*-gluconyl chloride pentaacetate. C. E. BRAUN, S. H. NICHOLS, jun., J. L. COHEN, and T. E. AITKEN (J. Amer. Chem. Soc., 1940, 62, 1619).—Prep. of this chloride from the acid pentaacetate by PCl_5 in Et_2O is improved (83—93% yield) and simplified. R. S. C.

Structure of trimethylglucurone. R. E. REEVES (J. Amer. Chem. Soc., 1940, 62, 1616—1617).—The trimethylglucurone (I), m.p. 129—130°, $[\alpha]_{\text{D}}^{20} +151^\circ$ in CHCl_3 , of Pryde *et al.* (A., 1933, 1035) is shown to be the 1:2:4-trimethylfuranoside. Its prep. from glucurone is improved to give a 50% yield. Mutarotation in 36% HCl—MeOH gives glucurone 2:5-dimethyl- β -methylglucoside, m.p. 90—91°, $[\alpha]_{\text{D}}^{20} +2.0^\circ$ in H_2O , -2.3° in CHCl_3 , the rapid rate in dil. acid being characteristic of methylfuranosides. Oxidation of (I) by HNO_3 (d 1.2) at 80—85° gives α -dimethylsaccharic acid, converted by CH_2N_2 into the unsaturated lactone, m.p. 85—86.5° (Schmidt *et al.*, A., 1938, II, 42), and by HCN—MeOH, followed by NH_3 —MeOH, into α -dimethylsacchardiamide, m.p. 169—170°. R. S. C.

Oxidation of alginic acid by periodic acid. H. J. LUCAS and W. T. STEWART (J. Amer. Chem. Soc., 1940, **62**, 1793—1796).—The structure of alginic acid (I) (A., 1939, II, 405) is confirmed. HIO_4 oxidises (I) to the product (II), $\cdot\text{CH}(\text{CHO})\cdot\text{O}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}(\text{CHO})\cdot\text{O}\cdot$ or $\cdot\text{CH}(\text{CHO})\cdot\text{O}\cdot\text{CH}(\text{CHO})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{O}\cdot$, oxidised by $\text{Br}\cdot\text{BaCO}_3\cdot\text{H}_2\text{O}$ to the tricarboxylic acid, hydrolysis of which by H_2O at 100° gives *meso*-tartaric acid (III) (25%) and $\text{H}_2\text{C}_2\text{O}_4$. Hydrolysis of (II) gives $(\text{CHO})_2$ (42%). *Me* alginate gives similarly the dialdehyde-ester, which gives 30% of $(\text{CHO})_2$, and the carbo-methoxy-dicarboxylic acid, from which (III) could not be isolated. HIO_4 - or HIO_3 -oxidation is improved by pptg. the org. products by $\text{Bu}^\gamma\text{OH}$. $\text{H}_2\text{C}_2\text{O}_4$ and (III) are separated by heating with an excess of BzCl at $100\text{--}150^\circ$, which decomposes $\text{H}_2\text{C}_2\text{O}_4$ and yields *meso*-($\text{OBz}\cdot\text{CH}\cdot\text{CO}$) $_2\text{O}$ (IV), m.p. 207° , or by treating with aq. CuSO_4 , adjusting to p_{H} 2, removing the $\text{CuC}_2\text{O}_4\cdot 0.5\text{H}_2\text{O}$ and then the Ba as BaSO_4 , and recovering the (III) as such or as *monobrucine* salt, m.p. 259° (decomp.), $[\alpha]_{\text{D}}^{20} -23^\circ$, whence (IV) may be prepared. R. S. C.

Photolysis of methyl ethyl ketone.—See A., 1940, I, 368.

Synthesis of 5:5-disubstituted hydantoins from s-dialkoxypropanones and related compounds. B. G. ROGERS and H. R. HENZE (J. Amer. Chem. Soc., 1940, **62**, 1758—1760).— $\beta\beta'$ -*Di-n-hexoxy*-, b.p. $141\text{--}142^\circ/3$ mm., -*n-heptoxy*-, b.p. $160\text{--}161^\circ/5$ mm., - β'' -ethyl-*n-hexoxy*-, b.p. $162\text{--}163^\circ/5$ mm., and -allyloxy-, b.p. $124\text{--}125^\circ/24$ mm., -*isopropyl* alcohol are prepared (method: Fairbourne *et al.*, A., 1931, 599). β -*Methoxy*- β' -*ethoxy*-, b.p. $56\text{--}57^\circ/8$ mm., and β -*methoxy*- β' -*n-propoxy*-*isopropyl* alcohol, b.p. $59\text{--}60^\circ/5$ mm., are described (prep.: *idem.*, A., 1932, 928). Oxidation of the alcohol affords $\alpha\beta$ -*di-n-hexoxy*-, b.p. $135\text{--}136^\circ/5$ mm., -*n-heptoxy*-, b.p. $187\text{--}188^\circ/10$ mm., and - β' -ethyl-*n-hexoxy*- (I), b.p. $162\text{--}164^\circ/5$ mm., -*acetone*, but $\alpha\beta$ -*diallyloxyacetone*, b.p. $118\text{--}120^\circ/24$ mm. (2:4-*dinitrophenylhydrazone*, m.p. $45\text{--}46^\circ$), is obtained only in poor yield. Condensation of $\text{OR}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OR}'$ with KCN and $(\text{NH}_4)_2\text{CO}_3$ in 50% EtOH at 100° gives 5:5-*di-methoxy*-, m.p. $214\text{--}215^\circ$, -*ethoxy*-, m.p. $180.5\text{--}181.5^\circ$, -*n-propoxy*-, m.p. $104.5\text{--}105.5^\circ$, -*n*-, m.p. $98.5\text{--}99.5^\circ$, -*iso*-, m.p. $173\text{--}174^\circ$, and -*sec-butoxy*-, m.p. $222\text{--}223^\circ$, -*n*-, m.p. $103.5\text{--}104.5^\circ$, and -*sec-amyl*oxy-, m.p. $146\text{--}147^\circ$, -*n-hexoxy*-, m.p. $82.5\text{--}84^\circ$, -*n-heptoxy*-, m.p. $71\text{--}73^\circ$, and -*allyloxy*-, m.p. $107.5\text{--}108.5^\circ$, -*methylhydantoin*, yields varying from 0.5 to 39%. $\text{CO}(\text{CH}_2\cdot\text{OP}^n)_2$ and (I) do not give a hydantoin. Temp. are corr. R. S. C.

Lignin and related compounds. XLVII. Synthesis of xylosides related to lignin plant constituents. J. H. FISHER, W. L. HAWKINS, and H. HIBBERT (J. Amer. Chem. Soc., 1940, **62**, 1412—1415; cf. A., 1940, II, 19).—Addition of acetobromoxylose (2 mols.) in COMe_2 to α -acetoxypropiovanillone (I) (prep. from the α -Br-ketone by $\text{KOAc}\cdot\text{AcOH}$ at 100°) (1 mol.), m.p. $105\text{--}106^\circ$, and *n*-KOH (0.1 mol.) and then gradually of aq. KOH to keep the $p_{\text{H}} = 9$ [90% neutralisation of the (I)] gives 25% of the β -*d-xyloside triacetate*, m.p. $149.4\text{--}149.7^\circ$, which

with $\text{NaOMe}\cdot\text{MeOH}$ at 20° gives α -*hydroxypropiovanillone* β -*d-xyloside*, m.p. $193\text{--}194.5^\circ$ (decomp.). α -*Acetoxypropiosyringone* β -*d-xyloside triacetate*, m.p. $128.6\text{--}128.8^\circ$, and α -*hydroxypropiosyringone* β -*d-xyloside*, m.p. $149.4\text{--}150^\circ$, unstable in hydroxylic solvents at 45° , are similarly prepared. Condensation without p_{H} control gives *guaiacol* β -*d-xyloside triacetate*, m.p. $139.8\text{--}140^\circ$, and *acetovanillone* β -*d-xyloside triacetate*, m.p. $133.3\text{--}133.6^\circ$, and thence ($\text{NaOMe}\cdot\text{MeOH}$ or aq. NH_3) *guaiacol*, m.p. $175.3\text{--}176^\circ$, and *acetovanillone*, m.p. $145.2\text{--}145.7^\circ$, β -*d-xyloside*. R. S. C.

Action of the pyridine-acetic anhydride reagent on *d*- α -glucoheptose-, *d*-glucosamine-, and *l*-fucose-oximes. E. R. DE LABRIOLA and V. DEULOFEU (J. Amer. Chem. Soc., 1940, **62**, 1611—1613).—The mode of reaction of $\text{C}_5\text{H}_5\text{N}\cdot\text{Ac}_2\text{O}$ with sugar oximes depends on the particular sugar and is only partly explicable. *d*- α -Glucoheptoseoxime, semi-cryst., and $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ (1:1) at -10° or 20° give *d*- α -glucoheptonitrile hexa-acetate, m.p. $113\text{--}114^\circ$, $[\alpha]_{\text{D}}^{20} +24.1^\circ$ in CHCl_3 . *d*- α -Glucosamineoxime hydrochloride (modified prep.), m.p. 166° , at -10° or 20° gives *d*-glucosamine nitrile penta-acetate, m.p. 126° (lit. $118\text{--}119^\circ$), $[\alpha]_{\text{D}}^{20} +20.5^\circ$ in CHCl_3 . *l*-Fucoseoxime at -10° gives only the oxime penta-acetate, but increasing amounts of *l*-fucosonitrile tetra-acetate, m.p. 177° , $[\alpha]_{\text{D}}^{20} -22.4^\circ$ in CHCl_3 , are formed as the reaction temp. rises until at 100° it is the main product. R. S. C.

Synthesis of trisaccharides. Their behaviour in alkaline solution. S. H. NICHOLS, jun., W. L. EVANS, and H. D. McDOWELL (J. Amer. Chem. Soc., 1940, **62**, 1754—1758).—Acetobromocellobiose, β -*d*-glucose 1:2:3:4-tetra-acetate, CaSO_4 , Ag_2O , and I in CHCl_3 give 45.4% of 6- β -cellobiosido- β -*d*-glucose hendeca-acetate (I), m.p. 246.5° (corr.), $[\alpha]_{\text{D}}^{24} -10.9^\circ$ in CHCl_3 . 6-*Mallosido*- β -*d*-glucose hendeca-acetate (II), m.p. $242\text{--}242.7^\circ$ (corr.), $[\alpha]_{\text{D}}^{24} +42.5^\circ$ in CHCl_3 . 6-*cellobiosido*- β -*d*-mannose hendeca-acetate (III), amorphous, softens at $120\text{--}126^\circ$ (corr.), $[\alpha]_{\text{D}}^{23} -18.4^\circ$ in CHCl_3 , and 6-*mallosido*- β -*d*-mannose hendeca-acetate (IV), amorphous, softens at $110\text{--}115^\circ$ (uncorr.), $[\alpha]_{\text{D}}^{23} +58.6^\circ$ in CHCl_3 , are also prepared. With $\sim 1.78\text{--}6.19\text{N}\cdot\text{KOH}$ at 50° (cf. Nadeau *et al.*, A., 1934, 173), (I) and (II) give approx. the amount of lactic acid (V) obtained similarly from 2 equivs. of glucose, and (III) and (IV) give approx. the amounts obtained from 1 equiv. of glucose + 1 equiv. of mannose. This supports the views of Evans *et al.* (A., 1930, 326) that (V) is to be expected only from the first and third hexose units. R. S. C.

Structure of dextran.—See A., 1940, III, 694.

Constitution of lichenin. IV. K. HESS and L. W. LAURIDSEN (Ber., 1940, **73**, [B], 115—126; cf. A., 1927, 860).—Lichenin (I), from *Cetraria islandica*, has a constitutional scheme similar to that of cellulose. With $\text{Me}_2\text{SO}_4\cdot\text{NaOH}$, (I) gives a product (41—43% OMe), which with $\text{MeI}\cdot\text{Ag}_2\text{O}$ gives *trimethyl-lichenin* (II) (45.5% OMe). By the terminal group method of Neumann *et al.* (A., 1937, II, 232), (II) yields tetramethyl- and 2:3:6-trimethyl-methylglucoside, with no dimethylglucose groups. Differ-

ences in $[\alpha]$ etc., however, show that the constitution of (I) is not identical with that of (II). It is suggested that in (I) the glucose groups are linked not only in the β 1-4, but also in the β 1- β 1 and 4-4, positions. Since (I) is hydrolysed enzymically completely to cellobiose (IV), it may be necessary to assume that the β 1- β 1 and 4-4 linkages are hydrolysed before the β 1-4 of (IV). Measurements of η in dioxan show that methyl-lichenin and -cellulose have very similar structural η , whereas methylstarch is about 100 times as sensitive to shear-strain.

E. W. W.

Optics of starch grains.—See A., 1940, I, 350.

Structure of cellulose. W. H. HAYFORD, jun. (Rayon Text. Month., 1940, 21, 355—356, 416—417).—A review.

R. J. W. R.

Preparation and properties of high mol. wt. primary amines.—See B., 1940, 513.

Manufacture of maltosamines.—See B., 1940, 513.

Pantothenic acid. V. Evidence for structure of the non- β -alanine portion. H. K. MITCHELL, H. H. WEINSTOCK, jun., E. E. SNELL, (MISS) S. R. STANBERY, and R. J. WILLIAMS. VI. Isolation and structure of the lactone moiety. E. T. STILLER, J. C. KERESZTESY, and J. FINKELSTEIN. VII. Partial and total synthesis. R. J. WILLIAMS, H. K. MITCHELL, H. H. WEINSTOCK, jun., and E. E. SNELL. VIII. Total synthesis of pure pantothenic acid. E. T. STILLER, S. A. HARRIS, J. FINKELSTEIN, J. C. KERESZTESY, and K. FOLKERS. IX. Biological activity of hydroxypantothenic acid. H. K. MITCHELL, E. E. SNELL, and R. J. WILLIAMS (J. Amer. Chem. Soc., 1940, 62, 1776—1779, 1779—1784, 1784—1785, 1785—1790, 1791—1792; cf. A., 1939, II, 461; 1940, II, 203).—V. The FeCl_3 test indicates $\text{OH}\cdot\text{C}\cdot\text{CO}_2\text{H}$ in pantothenic acid (I) after, but not before, hydrolysis by NaOH . This is confirmed by micro-determination of CO liberated by H_2SO_4 at 140° , the reaction being $\text{OH}\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{RCHO} + \text{HCO}_2\text{H} \rightarrow \text{CO} + \text{H}_2\text{O}$; the method is tested on α -hydroxy- γ -butyrolactone (II), $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III), and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (IV). FeCl_3 indicates absence of α -OH after hydrolysis by acid; this is due to lactonisation, an interpretation confirmed by titrations with alkali. Synthetic products are determined biologically by *Streptococcus lactis* (A), which is unaffected by excess of β -alanine (V) present. Absence of $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{H}$ is proved by dehydrating micro-quantities by H_2SO_4 and then titrating with KMnO_4 in COMe_2 ; the method is tested on α - and β -hydroxy- γ -butyrolactone, (III), (IV), erythrrolactone (VI), $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}(\text{OH})\cdot\text{CO}_2\text{H}$, $(\text{OH}\cdot\text{CH}_2)_2\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$, and α -hydroxy- β -methyl- γ -butyrolactone. (I) is recovered largely unchanged after treatment with $\text{Pb}(\text{OAc})_4$, HIO_4 , or NaOI . Condensation of (V) with α -hydroxy-valero-, α - or β -methyl- γ -butyrolactone gives very slightly active products, but products from (II) and (VI) are inactive. Prep. from liver extract of COMe_2 -insol. products containing 10—25% of Ba pantothenate is described, two adsorptions on C being essential steps. Acetyl-
Q** (A., II.)

ation of Ca pantothenate with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 100° and subsequent treatment with CH_3N_2 yields Me acetyl-pantothenate, a liquid, distils at 10^{-4} to 10^{-6} mm., hydrolysed (physiological test) by $\text{N-KOH}\cdot\text{EtOH}$ at room temp.

VI. Hydrolysis of nearly pure (I) gives oily lactones, but a prep. containing 10% of the Ba salt and free from lactonising OH-acids yields (—)- α -hydroxy- β -dimethyl- γ -butyrolactone (VII), m.p. $92\text{--}93^\circ$, sublimes at $25^\circ/10^{-4}$ mm., $[\alpha]_D^{25} -49.8^\circ$ in H_2O , the structure of which is proved by known and the following facts. (VII) contains 1 active H, gives an acetate, m.p. $41\text{--}42^\circ$, sublimes at $40^\circ/10^{-5}$ mm., 3:5-dinitro-, m.p. $156\text{--}157^\circ$, and p-nitrobenzoate, m.p. 112° . Kuhn-Roth determination shows 0.26 CMe, indicating $\text{C}\cdot\text{CMe}_2\cdot\text{C}$. $\text{N-NaOH}\cdot\text{EtOH}$ hydrolyses (VII) to a (+)-Na salt, $[\alpha]_D^{25} +22.19^\circ$ in ~50% aq. EtOH, lactonised by HCl at a rate suggesting a γ -lactone. Oxidation of the Ba salt by aq. BaMnO_4 (6 O) at 50° and p_H 8—8.5 $[\text{Ba}(\text{OH})_2]$ gives COMe_2 . With MgPhBr in Et_2O , (VII) gives α -diphenyl- γ -dimethyl-n-butane- $\alpha\beta$ -triol, m.p. $154\text{--}155^\circ$, oxidised by $\text{Pb}(\text{OAc})_4$ in C_6H_6 at 48° to COPh_2 , and with MgMeI gives $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, oxidised by $\text{Pb}(\text{OAc})_4$ in C_6H_6 at 50° to $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$, which is identified by oxidation by Ag_2O in aq. EtOH to $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Boiling 48% HBr does not affect (VII). Synthesis of (I) from natural and synthetic (VII) by condensation with β -alanine Et ester (VIII) and subsequent hydrolysis gives products of equal activity towards (A). (I) is, therefore,

$\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$.

VII. Hydrolysis of Ca pantothenate by 0.5N-HCl at 100° , re-esterification by (VIII) at $65\text{--}75^\circ$, and hydrolysis of the CO_2Et by 0.3N- Na_2CO_3 regenerates 43—49% of the biological activity of (I). Heating hydrolysed (I) with the Na salt of (V) in EtOH and *dl*-(VII) at $95\text{--}100^\circ$ gives a product showing 50% of the activity (*Lactobacillus casei* ϵ) of natural (I).

VIII. $\text{Pr}^\beta\text{CHO}$, 20% aq. CH_2O , and K_2CO_3 at $\geq 20^\circ$ give $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$, m.p. $96\text{--}97^\circ$, b.p. $83\text{--}86^\circ/15$ mm., which, when treated with aq. NaHSO_3 at 100° and then aq. KCN at $5\text{--}10^\circ$, gives the cyanohydrin, hydrolysed, first by Et_2O -conc. HCl at room temp. and then conc. HCl at 100° , to *dl*- α -hydroxy- β -dimethyl- γ -butyrolactone (IX), m.p. $56\text{--}58^\circ$, b.p. $119\text{--}121^\circ/15$ mm. (p-nitrobenzoate, m.p. $137\text{--}138^\circ$). Hydrolysis by NaOH at $80\text{--}90^\circ$ to the Na salt, neutralisation by HCl , and treatment with quinine hydrochloride gives quinine (+)- $\alpha\gamma$ -dihydroxy- $\beta\beta$ -dimethylbutyrate, m.p. 189° , $[\alpha]_D^{25} -130.5^\circ$ in MeOH, whence 2.5N-HCl at 100° gives the (—)-lactone (VII), m.p. $89\text{--}90^\circ$, $[\alpha]_D^{25} -50.7^\circ$ in H_2O (p-nitrobenzoate, m.p. 112°). The Ba salt from (IX) with quinine sulphate in H_2O gives BaSO_4 and then quinine (—)- $\alpha\gamma$ -dihydroxy- $\beta\beta$ -dimethylbutyrate, m.p. $176\text{--}178^\circ$, $[\alpha]_D^{25} -146^\circ$ in MeOH, and thence (+)- α -hydroxy- $\beta\beta$ -dimethyl- γ -butyrolactone, m.p. 91° , $[\alpha]_D^{25} +50.1^\circ$ in H_2O (p-nitrobenzoate, m.p. 114°). The (+)-lactone is racemised in H_2O at 150° or more slowly in boiling abs. EtOH. Heating the (—), (+), and *dl*-lactone with (VIII); hydrolysing the product with 0.45—0.9N- $\text{Ba}(\text{OH})_2$, and removing the Ba etc. gives pure, gummy (+)- (natural) (micro-cryst. Ca salt, $[\alpha]_D^{25}$

+24.27° in H₂O), (—)· (*Ca* salt, $[\alpha]_D^{25}$ —23.80° in H₂O), and *dl*-pantothenic acid (*Ca* salt; *benzylthiuronium* salt, m.p. 135—136°), respectively. Only thus is the natural acid obtained pure. The synthetic (+)-acid is identical with the vitamin in biological action on bacteria, chicks (15 or 20 mg. per 100 g. of diet produces twice the wt. increase of 10-mg. doses), and rats (one 0.8-mg. dose effective). The (—)-acid from pure (+)-lactone is ineffective (bacteria, rats) and the *dl*-acid has 47—52% of the activity of the vitamin.

IX. (OH·CH₂)₂CMe·CHO and a drop of NMe₃ in liquid HCN give a cyanohydrin, hydrolysed to α -hydroxy- β -methyl- β -hydroxymethyl- γ -butyrolactone, which with the Na salt of (V) gives "hydroxypantothenic acid,"

(OH·CH₂)₂CMe·CH(OH)·CO·NH·[CH₂]₂·CO₂H. Bioassay of (I) by yeast or bacteria gives results which vary greatly according to conditions of growth, but natural and synthetic (I) give identical results.

R. S. C.

Dialkylacetylbiurets. A. J. HILL and W. M. DEGNAN (J. Amer. Chem. Soc., 1940, **62**, 1595—1596).—RCOCl and AgNCO in Et₂O give α -ethyl-*n*-butyryl-, b.p. 59—61°/31 mm., α -ethyl-*n*-hexoyl-, b.p. 78—85°/20 mm., β -methyl- α -ethyl-*n*-valeryl-, b.p. 55—56°/11 mm., δ -methyl- α -ethyl-*n*-hexoyl-, b.p. 100—105°/30 mm., α -*n*-butyl-*n*-hexoyl-, b.p. 68—73°/12 mm., α -phenyl-*n*-butyryl-, b.p. 111—115°/11 mm., α -ethyl- Δ^7 -*n*-pentenoyl-, b.p. 83—85°/34 mm., $\alpha\alpha$ -dimethyl-*n*-butyryl-, b.p. 65—70°/10 mm., benzoyl-, b.p. 88—91°/20 mm., and phenylacetyl-, b.p. 116—120°/20 mm., -carbimide. With CO(NH₂)₂ or the appropriate derivative in boiling Et₂O these yield α -ethyl-*n*-butyryl-, m.p. 178°, α -ethyl-*n*-hexoyl-, m.p. 106°, β -methyl- α -ethyl-*n*-valeryl-, m.p. 89°, δ -methyl- α -ethyl-*n*-hexoyl-, m.p. 177°, α -*n*-butyl-*n*-hexoyl-, m.p. 158°, α -phenyl-*n*-butyryl-, m.p. 154°, α -ethyl- Δ^7 -*n*-pentenoyl-, m.p. 106°, benzoyl-, m.p. 233°, phenylacetyl-, m.p. 203°, $\alpha\alpha$ -dimethyl-*n*-butyryl-, m.p. 171°, α - α' -ethyl-*n*-butyryl- ϵ -ethyl-, m.p. 245°, α - α' -ethyl-*n*-butyryl- $\epsilon\epsilon$ -diethyl-, m.p. 104°, α - α' -ethyl-*n*-butyryl- $\epsilon\epsilon$ -pentamethylene- (I), m.p. 113°, and α - α' -ethyl-*n*-butyryl- ϵ - α' -phenyl-*n*-butyryl-, m.p. 127°, -biuret and ethylenedi- (ϵ - α' -ethyl-*n*-butyrylbiuret), m.p. 246°. α - α' -Ethyl-*n*-butyryl-, m.p. 132°, α - δ' -methyl- α' -ethyl-*n*-hexoyl-, m.p. 123°, and α - α' -ethyl- Δ^7 -*n*-hexenoyl-, m.p. 123°, - δ -thiobiuret are similarly prepared in C₆H₆. The biurets, especially (I), are potent hypnotics of low toxicity.

R. S. C.

Preparation of nitriles and amides. Reactions of esters with acids and with aluminium chloride. Use of the salt, NaCl·AlCl₃, in the Friedel-Crafts reaction. J. F. NORRIS and A. J. KLEMKA (J. Amer. Chem. Soc., 1940, **62**, 1432—1435).—Eleven nitriles are prepared in 63—97% yield by distilling the corresponding amide with AlCl₃·NaCl (prep. described) (cf. A., 1939, II, 372); a procedure applicable to 10 mg. is described. NH₄ salts give poorer yields and amides could not be isolated as intermediates. Amides are often conveniently prepared by heating NH₂Ac and the acid, so that AcOH distils off; this reaction is reversible, since BzOH and NHPhAc give NHPhBz. Inter-

change of ester groups occurs when BzOH is heated with PhOAc or EtOAc. AlCl₃·NaCl may be used in Friedel-Crafts reactions, but is less vigorous than AlCl₃. It yields CH₂Ph₂ from CH₂PhCl and C₆H₆, but does not cause reaction of C₆H₆ with CHCl₃ or CCl₄; it catalyses reaction with alkyl halides. Boiling NH₄Cl in BzCl gives PhCN, probably by way of NH₂Bz. EtOBz (1 mol.) and AlCl₃ (1 mol.) at 165° give 95% of EtCl 2 : 6 : 1·C₆H₅Cl₂·CO₂Et with AlCl₃ at 110—130° gives EtCl (91%) and 2 : 6 : 1·C₆H₅Cl₂·CO₂H, but with NH₂Ac at 200—210° gives only *m*-C₆H₄Cl₂ (28%). BzOH (1 mol.), PhMe (2), and AlCl₃ (2 mols.) give 60% of ketones, mainly *p*-C₆H₄Me·COPh.

R. S. C.

Manufacture of α -cyano- $\Delta^{\alpha\gamma}$ -butadiene.—See B., 1940, 515.

Equilibrium composition of magnesium *n*-butyl chloride solutions in ethyl ether. C. R. NOLLER and D. C. RANEY (J. Amer. Chem. Soc., 1940, **62**, 1749—1751).—Only small amounts of MgCl₂ are pptd. from MgBu⁺Cl in Et₂O, even if solid MgCl₂ is added to prevent supersaturation. Analysis of the equilibrium mixtures indicates 1.2% of MgEt₂. Thus, either the dioxan method of analysis (A., 1940, I, 116) is erroneous or the solubility of MgCl₂ is enormously increased by presence of MgBu⁺₂ and MgBu⁺Cl.

R. S. C.

Redistribution reaction. VIII. Relative affinity of mercury and lead for methyl and ethyl radicals. G. CALINGAERT, H. SOROOS, and G. W. THOMSON (J. Amer. Chem. Soc., 1940, **62**, 1542—1545; cf. A., 1940, II, 269).—2 : 1 HgEt₂·PbMe₄ or HgMe₂·PbEt₄ in presence of a little AlCl₃ at 78—83° give the same equilibrium mixture, due to random distribution, but containing more Me and less Et attached to the Hg to the Pb.

R. S. C.

Hindered rotation. I—III.—See A., 1940, I, 232.

Acetylenic cyclohexane derivatives. C. S. MARVEL, R. MOZINGO, and R. WHITE (J. Amer. Chem. Soc., 1940, **62**, 1880—1881).—The MgBr derivative (prep. by MgEtBr) of 2-methyl-1-acetylenylcyclohexanol with COMeEt in Et₂O gives 2-methyl-1- γ -hydroxy- γ -methyl- Δ^{α} -pentinenylcyclohexanol, m.p. 69—70°, dehydrated by KHSO₄ at 180° to 2-methyl-1- γ -methyl- α - Δ^{γ} -pentinenyl- Δ^1 -cyclohexene, b.p. 82—84°/2 mm. The MgBr derivative of 1-acetylenylcyclohexanol and 2-methylcyclohexanone give α -1-hydroxy-1-cyclohexyl- β -1'-hydroxy-2'-methyl-1'-cyclohexylacetylene, m.p. 94—95°, dehydrated by boiling 40% H₂SO₄ to α -1- Δ^1 -cyclohexenyl- β -2'-methyl-1- Δ^1 -cyclohexenylacetylene, b.p. 115—117°/2 mm.

R. S. C.

Spectrographic study of the formation of $\Delta^{1:3}$ -cyclohexadiene from cyclohexene. (MISSIS) H. STÜCKLEN, H. THAYER, and P. WILLIS (J. Amer. Chem. Soc., 1940, **62**, 1717—1719).—Traces of C₆H₆ and cyclohexadiene (I) can be detected spectrographically in cyclohexene (II) and are present in (II) as usually prepared. C₆H₆ is removed by fractionation, and (I) by interaction with (:CH·CO)₂O, excess of the anhydride being then removed by filtration at —78°. The absorption spectrum of pure (II) is reported. Illumination (ultra-violet) of (II) in N₂

causes formation of (I), increased if peroxide or aldehyde is present. In sunlight- N_2 , (II) containing a trace of peroxide slowly gives a gummy polymeride of (I). Distillation of (II) causes gradual formation of (I).

R. S. C.

Calculation of dipole moments from rates of nitration of substituted benzenes.—See A., 1940, I, 347.

Hydrogen fluoride as a condensing agent. XI. Reaction of alcohols and ethers with benzene. J. H. SIMONS and S. ARCHER. XII. Reactions of methyl, ethyl, and phenyl compounds with benzene and its derivatives. J. H. SIMONS and H. J. PASSINO (J. Amer. Chem. Soc., 1940, 62, 1623—1624, 1624; cf. A., 1940, II, 168).—XI. *sec.* and *tert.* Alcohols condense with C_6H_6 in HF at room temp., but for primary alcohols 100° is usually necessary. Bu^oOH or Bu_2O gives $\sim 20\%$ of $CHPhMeEt$. $CH_2Ph\cdot OH$ or $(CH_2Ph)_2O$ at room temp. gives 65—70% of CH_2Ph_2 . Pr^oOH or Pr^o_2O with C_6H_6 (1:7) gives $PhPr^o$ (22.4, 26), $p-C_6H_4Pr^o$ (14, 24), 1:2:4- $C_6H_3Pr^o_3$ (24, 25), and 1:2:4:5- $C_6H_2Pr^o_4$ (28, 8%, respectively). Bu^oOH or $CMc_2Et\cdot OH$ with C_6H_6 (1:7) gives 40% of mono- and 50% of dialkylated products. The fact that alcohols give higher yields than do chlorides is connected with evolution of H_2O in solution in HF from the former and of HCl at 1 atm. from the latter. Condensations by HF and $AlCl_3$ proceed by different mechanisms.

XII. $EtOH$ and C_6H_6 in HF at 200° give high yields of $PhEt$ and $C_6H_4Et_2$. EtI , $ClCO_2Et$, $EtOAc$, and Et_2O condense with C_6H_6 and $PhMe$ in HF. C_2H_4 at 0° gives \times traces of $PhEt$. $MeOH$, $MeOAc$, and MeI do not condense with C_6H_6 , $PhMe$, or $PhOH$ in HF at 200° , but $PhOH$ and $MeOH$ in HF give $PhOMe$. $PhOH$, $PhCl$, and Ph_2O do not give phenylated products at 200° ; $PhOAc$ and C_6H_6 give some $COPhMe$ and $PhOH$. $EtOH$ and $PhOH$ give no $PhOEt$, but Ph_2O alone in HF gives a little $PhOH$. Little tar is formed, except sometimes with $PhOH$. No details are given.

R. S. C.

Intermediate complexes in the Friedel-Crafts reactions. J. F. NORRIS and J. E. WOOD, III (J. Amer. Chem. Soc., 1940, 62, 1428—1432).—Compounds, $2AlBr_3\cdot s-C_6H_3Et_3\cdot HBr$ (I) (cf. A., 1940, II, 270), $2AlBr_3\cdot s-C_6H_3Me_3\cdot HBr$ (II), $2AlBr_3\cdot s-C_6H_3Et_3\cdot EtBr$, and $2AlBr_3\cdot s-C_6H_3Me_3\cdot EtBr$, are prepared from appropriate amounts of the components. Little reaction occurs between CO_2 and $2AlBr_3\cdot 2s-C_6H_3Et_3\cdot HBr$, $2AlBr_3\cdot 3s-C_6H_3Me_3\cdot HBr$, or (II), but CO_2 , $s-C_6H_3Me_3$ (1 mol.), and $AlBr_3$ (1 mol.) give $CO(s-C_6H_3Me_3)_2$ (44.9%) and $s-C_6H_3Me_3\cdot CO_2H$ (26.9%). Addition of HBr increases 1000-fold the conductivity of $AlBr_3$ in $PhMe$. Electrolysis of (I) involves transfers, which are most simply interpreted as due to a salt, $[C_6H_3Et_3\cdot H]Al_2Br_7$. Passage of HBr or HCl into $2AlCl_3\cdot PhNO_2$ or $AlBr_3\cdot PhNO_2$, respectively, involves mainly replacement of halogen (use of HI leads to some $C_6H_2I_3\cdot NH_2$); similar replacements occur with C_6H_6 and $PhMe$. $2AlHal_3\cdot PhNO_2$ are oxidising agents, which may explode under certain conditions. C_6H_6 , $AcCl$, and $AlBr_3$ give 70% of HBr ; C_6H_6 , $AcBr$, and $AlCl_3$ give 77% of HCl .

R. S. C.

Polymethylbenzenes. XXVI. Nitration of bromopentamethylbenzene. L. I. SMITH and J. W. HORNER, jun. (J. Amer. Chem. Soc., 1940, 62, 1349—1354; cf. A., 1940, II, 224).—Elimination of Me on nitration of polymethylbenzenes occurs by way of substituted benzyl nitrates. C_6Me_5Br and HNO_3 (d 1.5) in $CHCl_3$ at -11° to -1° give an oil, which in $MeOH$ yields a 3:2 mixture (A) of 2:3:4:6:5:1- and 2:3:4:5:6:1- $C_6Me_4Br\cdot CH_2\cdot O\cdot NO_2$ with some derived $C_6Me_4Br\cdot OMe$. More vigorous conditions give some 1:2:3:4:5:6- $C_6Me_5Br(NO_2)_2$. Conversion of (A) by boiling $KOH-EtOH$ into the Et ethers, by $H_2SO_4-AcOH-H_2O$ into the dibenzyl ethers, by $Ac_2O-H_2SO_4$ into the acetates, by aq. $COMe_2$ at $200-240^\circ$ into the alcohols, and by boiling $HCl-EtOH$ into the chlorides is described. Conversion of the acetates into the dibenzyl ethers, alcohols, and chlorides, of the alcohols and dibenzyl ethers into the chlorides, of the chlorides into the iodides, and of the iodides into (A) is also described. Conc. H_2SO_4 at room temp. converts (A) into mixed $C_6Me_4Br\cdot NO_2$, reduced by $Sn-HCl$ to 1:2:3:4:5- $C_6HMe_4\cdot NH_2$ (I) and bromoaminoisodurene (II), m.p. $145.5-147^\circ$. 1:2:4:5:3- C_6HMe_4Br and CH_2O in HCl at 100° give 4-bromo-2:3:5:6-tetramethylbenzyl chloride, m.p. $105.5-107.5^\circ$, converted by $NaI-COMe_2$ at room temp. into the iodide, m.p. $118.5-120^\circ$, which with $KOAc$ in boiling $AcOH$ gives the acetate, m.p. $119.5-122^\circ$. With $AgNO_3$ in boiling dioxan this gives the nitrate, m.p. $113-114.5^\circ$. 1:2:3:5:4- C_6HMe_4Br gives similarly 5-bromo-2:3:4:6-tetramethylbenzyl chloride, m.p. $114-114.5^\circ$, iodide, m.p. $132.5-134^\circ$, acetate, m.p. $88.5-90^\circ$, and nitrate, m.p. $105-106.5^\circ$, and 1:2:3:4:5- C_6HMe_4Br gives 6-bromo-2:3:4:5-tetramethylbenzyl chloride, m.p. $114-116^\circ$, iodide, m.p. $142-143.5^\circ$, acetate, m.p. $96.5-98^\circ$, and nitrate, m.p. $90-92.5^\circ$. HNO_3 (d 1.5) in $CHCl_3-H_2SO_4$ converts the bromohydrocarbon into bromo-nitro-durene, m.p. $179-180^\circ$, -isodurene, m.p. $176.5-177.5^\circ$, and -prehnitene, m.p. $180-181.5^\circ$, reduced by $Sn-HCl$ to aminodurene, (II), and (I), respectively.

R. S. C.

Side-chain bromination. J. R. SAMPEY, F. S. FAWCETT, and B. A. MOREHEAD (J. Amer. Chem. Soc., 1940, 62, 1839—1840).—The rate of side-chain bromination in sunlight is $CH_2Ph_2 > s-C_6H_3Me_3 > C_6Me_6 > p-, m-, o\text{-xylene} > PhMe > p-, m-, o-C_6H_4MeCl > p-, m-, o-C_6H_4MeBr > p-, m-, o-C_6H_4MeI$; $o-, m-, p-C_6H_4Me\cdot CN$, $o-, m-, p-C_6H_4Me\cdot NO_2$, 1:2:4- $C_6H_3Me(NO_2)_2$, 1:2:4:6- $C_6H_2Me(NO_2)_3$, $CH_2(C_6H_4\cdot NO_2-p)_2$, and $p-C_6H_4Me\cdot SO_2Cl$ do not react. Under illumination by electric light, the rate varies greatly according to the solvent and its purity; e.g., presence of S in CS_2 or washing $CHCl_3$ with H_2O decreases the rate. $CHCl_3$ at 57° is itself brominated. Rates are recorded for the following substitution products of $PhMe$: in CS_2 at 57° $H > p- > o- > m-Cl > p- > m- > o-Br > p-I > p-CN > m-I > p-NI_2 > m-CN > o-I > m-NO_2 > o-CN > o-NO_2$; in CCl_4 at 57° $H > p-SO_2Cl, m-CO_2H > o-CO_2H > 2:4-(NO_2)_2 > 2:4:6-(NO_2)_3$ (unaffected); in CS_2 at 10° $\alpha-Ph > Me_5 > 3:5-Me_2 > p-Me > o- > m-Me > H$. Br in the side-chain is determined by removal by $NaOAc$ in boiling abs. $EtOH$ and titration of the $NaBr$ formed. Usually $>93\%$ of the Br introduced is in the side-chain.

R. S. C.

Reaction of organic halides with piperidine. V. Negatively substituted ethyl bromides. E. L. FOREMAN and S. M. McELVAIN (J. Amer. Chem. Soc., 1940, **62**, 1435—1438).—The reaction mechanism, $\text{CHXBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{piperidine} \rightarrow$

$\text{CHXBr} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \rightarrow \text{CHX} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$ etc. (A., 1934, 532), is confirmed since increasing the electronegativity of Y in $\text{C}_6\text{H}_4\text{Y} \cdot [\text{CH}_2]_2 \cdot \text{Br}$ (Y = o- or p- NO_2 , p-CN, p-Ac, p- CO_2Et , or H) increases the reactivity. This increase is accompanied by decrease in the amount of *tert.* amine formed by subsequent addition (residue remains as olefine), indicating a different mode of formation for the latter. β -Bromopropiophenone (prep. from $\text{Br} \cdot [\text{CH}_2]_2 \cdot \text{COCl}$ etc.), m.p. 58—59°, β -o-nitrophenylethyl (by nitration of $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{Br}$), m.p. 36—38°, b.p. 115—120°/0.5 mm., β -p-acetylphenylethyl (I) (by a Friedel-Crafts reaction), b.p. 117—118°/0.1 mm., β -p-carboxyphenylethyl [by oxidation of (I)], m.p. 205—207° (Et ester, b.p. 111—114°/0.1 mm.), and p-cyanophenylethyl bromide (prep. from the amide by SOCl_2), m.p. 49—50°, are described.

R. S. C.

Free radicals and radical stability. X. Influence of the methyl group on the stability of triphenylmethyl. S. T. BOWDEN and D. L. CLARKE (J.C.S., 1940, 883—887).—Diphenyl-o-tolylmethyl chloride [FeCl_3 , m.p. 137—138° (decomp.), and ZnCl_2 compound (an oil)] yields with Mg and CO_2 in Et_2O , diphenyl-o-tolylacetic acid, m.p. 226°, and with mol. Ag, $\text{CPh}_2 \cdot \text{C}_6\text{H}_4\text{Me}$. This shows less tendency to isomerise than methyltriphenylmethyis hitherto prepared, has (freshly prepared) a mol. wt. in C_6H_6 corresponding with a stability of 20%, and in PhBr absorbs 103—107% of the theoretical amount of O_2 , giving the peroxide, m.p. 164° (also prepared by the action of Hg on solutions of the chloride). Theories concerning the stability of such radicals are discussed.

A. LI.

Hexa-p-alkylphenylethanes. X. p-cyclohexyl derivatives of hexaphenylethane. C. S. MARVEL and C. M. HIMEL (J. Amer. Chem. Soc., 1940, **62**, 1550—1553; cf. A., 1939, II, 538).—Bromophenylcyclohexane, prepared from PhBr, cyclohexene, and AlCl_3 (Mayes *et al.*, A., 1929, 550; Brown *et al.*, A., 1937, II, 373), is a mixture of isomerides, since (a) interaction with Mg in Et_2O and then with CO_2 gives acids, which by dehydrogenation (Pd-C; 300°) yield o- $\text{C}_6\text{H}_4\text{Ph} \cdot \text{CO}_2\text{H}$, (b) with HNO_3 it gives p- (I) and m- $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO}_2\text{H}$, and (c) with CrO_3 in 50% AcOH it gives (I). p-Bromophenylcyclohexane (II), b.p. 110°/1.5—2 mm., is obtained from cyclohexylbenzene by Br and Fe (85% yield) or by treating the p-diazonium bromide in 40% HBr with Cu-bronze. p-Aminophenylcyclohexane is obtained (97%) from the NO_2 -compound by H_2 -Raney Ni. The Mg derivative (prep. with aid of a little MgEtBr) of (II) with COPh_2 , EtOBz , or Et_2CO_3 in C_6H_6 gives diphenyl-p-cyclohexylphenylcarbinol (65%), m.p. 95—96° (Et ether, m.p. 106—107°), phenyldicyclohexylphenylcarbinol (30%), m.p. 102—103° (Et ether, m.p. 152—153°), and tri-p-cyclohexylphenylcarbinol (35%), m.p. 180—181° (lit. 168°) (Et ether, m.p. 189—190°) (with a little pp'-dicyclohexylbenzophenone), respectively. With AcCl in boiling C_6H_6 , these give diphenyl-p-cyclo-

hexylphenyl-, m.p. 126—127° (lit. 123°), phenyldi-p-cyclohexylphenyl-, m.p. 155—156°, and tri-p-cyclohexylphenyl-, m.p. 169—170°, methyl chloride, which with Ag in C_6H_6 give solutions of tetraphenyldi- (III), diphenyltetra- (IV), and hexa- (V) -p-cyclohexylphenylethane and thence the derived peroxides, m.p. 158—159° (lit. 164°), 120—121°, and 178—179°, respectively. Magnetic susceptibility shows the following % dissociation in C_6H_6 at 25°: (III) $9 \pm 1\%$ (0.1M.), (IV) $10 \pm 1\%$ (0.1M.), (V) $50 \pm 7\%$ (0.01M.; equiv. to 22% in 0.08M. solution).

R. S. C.

Magneto-chemical investigation of organic substances. XVIII. True diradical with p-“free valencies.” E. MÜLLER and E. TIETZ (Naturwiss., 1940, **28**, 189—190; cf. A., 1940, II, 122).—2 : 6 : 2' : 6' -Tetrachloro-4 : 4' -di(phenyl-p-diphenylmethylenediphenyl, ($p\text{-}\dot{\text{C}}_6\text{H}_4\text{Ph} \cdot \dot{\text{C}}\text{Ph} \cdot \text{C}_6\text{H}_4\text{Cl}_2$) $_2$), is shown by its paramagnetism to exist partly as diradical, the structure being due to hindrance by the o-Cl of free rotation of the central $\text{C}_6\text{-C}_6$ linking. As in the CPh_3 series, introduction of $\text{C}_6\text{H}_4\text{Ph}$ for Ph increases the degree of dissociation.

R. S. C.

Polymethyl aromatic hydrocarbons. I. Synthesis of 1 : 2 : 4-tri-, 1 : 2-, 1 : 3-, and 1 : 4-dimethylnaphthalene. M. C. KLOETZEL (J. Amer. Chem. Soc., 1940, **62**, 1708—1713).—72—98% yields are obtained throughout the syntheses.

$\text{Bz} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{Me}$ (prep. from the acid by $\text{MeOH} \cdot \text{H}_2\text{SO}_4$), b.p. 132°/0.4 mm. (semicarbazone, m.p. 138—139°), and MgMeI under defined conditions give 75% of $\text{CPhMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (cf. Mayer *et al.*, A., 1923, i, 802), hydrogenated (PtO_2 ; 0.5 atm.; AcOH) to $\text{CHPhMe} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$, b.p. 165—166°/12 mm., which in 80% H_2SO_4 gives 1-keto-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I), b.p. 110—111°/1 mm. [semicarbazone, m.p. 209—211° (lit., 210°, 204°)]. With MgMeI in boiling Et_2O this gives 1-hydroxy-1 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 82—82.5°, dehydrated by HCO_2H , first boiling (1 min.) and then at 25°, to 1 : 4-dimethyl-1 : 2-dihydronaphthalene, b.p. 87—88°/0.8 mm. With Pd-C at 260—280°, later 280—290°, this gives 1 : 4- $\text{C}_{10}\text{H}_6\text{Me}_2$, b.p. 108—109°/1 mm. [picrate, m.p. 143—144°; styphnate, m.p. 125—126°; s- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 165—166°]. $\text{Me}_2\text{C}_2\text{O}_4$ condensed with (I) gives the 2-glyoxylate, which with glass powder at 175—185° gives Me 1-keto-4-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate, m.p. 66—67°, b.p. 150—152°/2 mm. $\text{MeI} \cdot \text{NaOMe}$ then yields Me 1-keto-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate, b.p. 158—159°/2 mm., hydrolysed at 50—55° by NaOH in H_2O containing a little EtOH to the acid, which, when distilled in steam, gives 1-keto-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (II), b.p. 112°/1 mm. [semicarbazone, m.p. 218—220° (decomp.)]. Clemmensen reduction of (II) gives 1 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 78°/1 mm., which with S at 230—240°, later 250—270°, or Pd-C at 200—250°, later 280—320°, gives 98 and 74%, respectively, of 1 : 3- $\text{C}_{10}\text{H}_6\text{Me}_2$, b.p. 117°/2 mm. [picrate, m.p. 117—118° (lit., 118°, 88—89°); styphnate, m.p. 116—118°]. With MgMeI in Et_2O , (II) gives 1-hydroxy-1 : 2 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 84—86°, and thence (HCO_2H)

1 : 2 : 4-trimethyl-3 : 4-dihydronaphthalene, b.p. 86—88°/0.4 mm., and 1 : 2 : 4- $C_{10}H_5Me_3$ (III), m.p. 54—55° (lit., 50°), b.p. 125—126°/0.6 mm. (picrate, new m.p. 148—148.5°; styphnate, m.p. 123.5°). The structure of (III) is confirmed as follows. $OH \cdot CPhMe \cdot CHMe \cdot CO_2Et$ (prep. by a Reformatsky reaction) with $KHSO_4$ gives an ester, hydrolysed to $CHPh \cdot CMe \cdot CO_2H$. $H_2 \cdot PtO_2$ in $AcOH$ reduces this to β -phenyl- α -methyl- n -butyric acid, m.p. 131—132°, b.p. 124—125°/0.2 mm., the chloride of which with CH_2N_2 gives the diazo-ketone and thence by Ag_2O in aq. $Na_2S_2O_3$ $CHPhMe \cdot CHMe \cdot CH_2 \cdot CO_2H$. Cyclisation by 80% H_2SO_4 then yields 1-keto-3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 96—97°/0.3 mm., which with $MgMeI$ in boiling Et_2O gives the carbinol, converted by dehydration (HCO_2H) and dehydrogenation (S; 220—230°) into (III). Me 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate gives (method as above) 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 115—116°/2.5 mm. [semicarbazone, m.p. 203—205° (lit. 199—201°, 200—201°)], and thence 1-hydroxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetra-, m.p. 65.5—66° (lit. 64—66°), and 1 : 2-dimethyl-3 : 4-di-hydronaphthalene, b.p. 101°/2.5 mm., and 1 : 2- $C_{10}H_6Me_2$ [picrate, m.p. 130—131°; styphnate, m.p. 142—143°; $s\text{-}C_6H_3(NO_2)_3$ derivative, m.p. 147—148°]. R. S. C.

Preparation of 2-phenylnaphthalene from diphenyl. D. H. HEY and R. WILKINSON (J.C.S., 1940, 1030).—The method is the same as that of Weizmann *et al.* (A., 1940, II, 253), except that cyclisation is accomplished by boiling with P_2O_5 in C_6H_6 and treating with ice- H_2O . A. LI.

Chelation of potassium compounds of carboxylic and sulphinic acids. W. G. WRIGHT (J.C.S., 1940, 859—862; cf. A., 1938, II, 478).— β - $C_{10}H_7 \cdot CO_2H$ with KOH (0.5 equiv.) in $EtOH$ yields the KH salt, $C_{11}H_8O_2 \cdot C_{11}H_7O_2K$, which chars without melting at a high temp. When α - $C_{10}H_7 \cdot CO_2H$ is treated with 0.5 KOH in $EtOH$ and the solution immediately evaporated, a mixture of three chelated H salts is produced: AS (A = acid, S = normal salt), m.p. 163°, AAS , m.p. 115°, and ASS , m.p. 175°. AS is obtained alone by evaporating the same solution after keeping for 2 days; AAS is also prepared by treating A with 0.5 KOH in C_6H_6 , or with $\frac{1}{2}$ KOH in $EtOH$, and a mixture of AAS and ASS by treating A with $\frac{1}{4}$ KOH + K_2CO_3 in C_6H_6 . ASS in $COMe_2$ + $CHCl_3 \rightarrow AS + S$ (pptd.); $AS + A$ in $COMe_2$ + $CHCl_3 \rightarrow AAS$; AS in $COMe_2$ + $CHCl_3$ (on long keeping) $\rightarrow AAS + S$ (pptd.); AS in $C_6H_6 \rightarrow AAS + ASS$ (pptd.). The sharp m.p., varying solubilities, and effects of recrystallisation confirm that these are definite compounds. $PhSO_2H$ and p - $C_6H_4Me \cdot SO_2H$ with 0.5 KOH in $EtOH$ yield KH salts which char without melting at a high temp. p - $C_6H_4Me \cdot SO_2H$ crystallises from $CHCl_3$ as a monohydrate, but melts under hot $CHCl_3$, the (chelated?) melt on resolidification giving an anhyd. salt which cannot be remelted in air. A. LI.

meso-Alkylanthracenes. L. F. FIESER and T. G. WEBBER (J. Amer. Chem. Soc., 1940, 62, 1360—1362).—1 : 2 : 3- $C_6H_3Me_3 \cdot CO \cdot C_6H_4 \cdot CO_2H \cdot o$ [prep. in 30% yield from 1 : 2 : 3- $C_6H_3Me_3 \cdot MgBr$ and o -

$C_6H_4(CO)_2O$ in $Et_2O \cdot C_6H_6$], m.p. 132—133°, solidifies, remelts at 139.5—140.5° (lit., m.p. 126—127°), with Zn dust in boiling 2N- $NaOH$ gives 94% of o -2 : 3-dimethylbenzylbenzoic acid, m.p. 177.2—177.8° (with some of the lactone, m.p. 127—128°, of o - α -hydroxy-2 : 3-dimethylbenzylbenzoic acid), which with $ZnCl_2$ in boiling $Ac_2O \cdot AcOH$ gives 1 : 2-dimethyl-10-anthranyl acetate, m.p. 158.1—158.7°. With $MgBu^aBr$ in C_6H_6 this is hydrolysed to 1 : 2-dimethylanthr-10-one (55%), m.p. 170.3—171.3°, which with $MgMeBr$ in boiling $Et_2O \cdot C_6H_6$ yields 1 : 2 : 10-trimethylanthr-10-one (77%), m.p. 90.6—91.4° [picrate, m.p. 138.5—139.5°; $s\text{-}C_6H_3(NO_2)_3$ compound, m.p. 169.6—170.2°; dimeride, m.p. 222—226°, formed by irradiation in $EtOH$]. α -Naphthaquinone (I) and $(CH_2 \cdot CMe)_2$ in boiling $EtOH$ give 95% of 2 : 3-dimethyl-1 : 4 : 9a : 4a-tetrahydroanthraquinone, m.p. 148.5—149.1°, converted by $MgMeI$ in $Et_2O \cdot C_6H_6$ into a diol, which is dehydrated at 140° to give 2 : 3 : 9 : 10-tetramethyl-1 : 4-dihydroanthracene (42%), m.p. 175.3—176.3° [picrate, m.p. 149.2—149.9°; $s\text{-}C_6H_3(NO_2)_3$ compound, m.p. 150.8—151.8°]. With S at 325° (55%) or $Pd \cdot C$ (25%) this gives 2 : 3 : 9 : 10-tetramethylanthr-10-one, m.p. 139.4—140.2° [dimeride, m.p. ~270°, formed by irradiation and partly dissociated at 210°/2 mm.; picrate, m.p. 177.3—177.8°; $s\text{-}C_6H_3(NO_2)_3$ compound, m.p. 188.8—189.3°]. $CHMe \cdot CMe \cdot CH \cdot CH_2$ (modified prep.) and (I) in boiling $EtOH$ give 1 : 2-dimethyl-1 : 4 : 9a : 4a-tetrahydroanthraquinone (81%), m.p. 101—101.7°, which with $MgMeCl$ gives only 1 : 2-dimethylanthr-10-one, m.p. 157.8—158.2° (lit. 156°), and with $MgMeI$ gives a substance, m.p. 140—154°. M.p. are corr. R. S. C.

Physico-chemical properties of 3 : 4-benzopyrene. F. WEIGERT and J. C. MOTTRAM (Nature, 1940, 145, 895—896).—Needles of commercial benzopyrene (I) emit a green fluorescence. The colloidal suspension obtained by pouring a solution of the green form of (I) in $COMe_2$ into H_2O emits a yellowish fluorescence. Heating the green form in a vac. gives a white sublimate, which fluoresces with a blue light. The green and blue forms are enantiomorphous modifications of (I) with a triple point at ~66°. The yellow form changes into the blue on keeping the colloidal suspension for several hr. at 100°, and into the green, at room temp. on moistening the dry residue from the evaporated suspension with $C_5H_{11} \cdot OAc$. The blue form is stabilised temporarily in presence of cholesterol. A similar stabilisation may occur in cells coming in contact with (I), and may make free energy available for biological action. L. S. T.

Phenyldimethylethylammonium bromide. A. KANT (J. Amer. Chem. Soc., 1940, 62, 1880).—This substance, m.p. 193—194°, is prepared from $NPhMe_2$ and $EtBr$. R. S. C.

Hydration of anilides of normal fatty acids.—See A., 1940, I, 360.

Breakdown of the sulphanilamide molecule by ultra-violet irradiation or chemical oxidation. S. M. ROSENTHAL and H. BAUER (Science, 1940, 91, 509; cf. A., 1938, III, 829; 1939, III, 710).—Ultra-violet irradiation of dil. aq. sulphanilamide (I) gives NH_3 and SO_4^{--} . The most effective $\lambda\lambda$ are those

<270 mμ. The amount of S split off increases regularly with the time of irradiation, but a change in concn. of (I) from 20 to 100 mg.-% has little effect for exposures of 10 min. Irradiation of the *o*- (II) and *m*- (III) -isomerides of (I) does not produce NH₃ and SO₄²⁻; sulphanilic acid (IV) liberates some NH₃. Oxidation of dil. aq. (I) by FeCl₃ and H₂O₂ also gives NH₃ and SO₄²⁻; the amount of the latter depends on the [Fe³⁺]. (II), (III), and (IV) react similarly.

L. S. T.

Sulphanilamide derivatives. VII. N¹-Alkane-sulphonylsulphanilamides and related compounds. M. L. CROSSLEY, E. H. NORTHEY, and M. E. HULTQUIST (J. Amer. Chem. Soc., 1940, **62**, 1415—1416; cf. A., 1940, II, 164).—Gradual addition of 50% aq. NaOH (to maintain *p*_H at 11—12) to RSO₂Cl and *p*-NHAc·C₆H₄·SO₂·NH₂ in H₂O at 35—40° and subsequent hydrolysis of the Ac by boiling aq. NaOH gives N¹-ethane-, m.p. 206.5—207.5°, -*n*-butane-α-, m.p. 209—210.5°, -*n*-pentane-α-, m.p. 183—184.5°, -β-ethyl-*n*-hexane-α-, m.p. 189—191°, -*n*-dodecane-α-, m.p. 188.8—189.9°, -cyclohexane-, m.p. 230° (decomp.), -dl-camphor-10-, m.p. 213—214.5°, and -toluene-ω-, m.p. 242—243.5°, -sulphonylsulphanilamide, which are only slightly effective against β-haemolytic streptococci in mice.

R. S. C.

Substituted sulphanilamides. II. N¹- and N⁴-Sulphonyl derivatives. J. M. SPRAGUE, L. F. MCBURNEY, and L. W. KISSINGER (J. Amer. Chem. Soc., 1940, **62**, 1714—1716).—RSO₂Cl and *p*-NH₂·C₆H₄·SO₂·NH₂ in boiling C₅H₅N give 41—73% yields of *p*-RSO₂·NH·C₆H₄·SO₂·NH₂, but in 10% aq. NaOH give 25—31% of *p*-NH₂·C₆H₄·SO₂·NH·SO₂R (A) (also obtained from the NO₂-compounds by H₂-PtO₂). The N⁴-derivatives of (A) are obtained by RCOCl in C₅H₅N or aq. alkali and from *p*-R'CO·NH·C₆H₄·SO₂·NH₂ by RSO₂Cl in 10% NaOH. Thus are obtained N⁴-methane-, m.p. 180—181°, N⁴-ethane-, m.p. 175—176°, N⁴-butane-α-, m.p. 160—161°, N⁴-pentane-α-, m.p. 156—156.5°, N⁴-hexane-α-, m.p. 153—153.5°, N⁴-dodecane-α-, m.p. 157—158°, N⁴-toluene-ω-, m.p. 226—227°, N⁴-benzene-, m.p. 147—148°, N¹-butane-α-, m.p. 205—206°, N¹-pentane-α-, m.p. 179—180°, N¹-toluene-ω-, m.p. 226—227°, N⁴-acetyl-N¹-pentane-α-, m.p. 202.5—203.5°, N⁴-*n*-hexoyl-N¹-pentane-α-, m.p. 152.5—153°, and N⁴-*n*-hexoyl-N¹-butane-α-, m.p. 182—183°, -sulphonylsulphanilamide. Bu⁴SO₂·NHPh and ClSO₃H at <20° give 67% of Bu⁴SO₂Cl; EtSO₂·NHPh gives similarly 20% of EtSO₂Cl, and PhSO₂·NHPh gives 71% of PhSO₂Cl. However, at 0—8°, *p*-butane-α-, m.p. 126—128°, *p*-ethane-, m.p. 127—128°, and *p*-benzene-sulphonamidobenzenesulphonyl chloride (4%) are obtained. *p*-Nitrobenzenesulphonbutane-α-sulphonamide, m.p. 117—118.5°, is prepared from *p*-NO₂·C₆H₄·SO₂·NH₂ and Bu⁴SO₂Cl in 10% NaOH.

R. S. C.

Quantitative hydrogenation of substituted azo-compounds in presence of Raney nickel at normal temperature and pressure. W. F. WHITMORE and A. J. REVUKAS (J. Amer. Chem. Soc., 1940, **62**, 1687—1693).—Hydrogenation of phenolic or acid azo-dyes in presence of Raney Ni in EtOH or dioxan at 1 atm. gives the two amines, usually in good yield, without affecting CHO, Ac, OMe, or Cl (cf. B., 1937,

1180). NO₂ is simultaneously reduced to NH₂ and attempts to isolate NO₂-amines after partial reduction failed. Reaction is faster in EtOH than in dioxan, but complications, e.g., formation of Schiff's bases from aldehydic dyes, may occur in EtOH. Cl-dyes are reduced faster than are NO₂-dyes, provided other groups are absent. Addition of a little excess of NaOH does not cause reduction of Ac, but accelerates the normal reduction of N:N. In presence of 2 mols. of NaOH in EtOH (not dioxan) reduction of N:N in Cl-dyes is accompanied by removal of Cl, and Cl may be thus determined either by measurement of the H₂ absorbed or by titration of the NaCl formed. However, Cl is eliminated from 2:1-OH·C₁₀H₆·N:N·C₆H₂MeCl·SO₃Na-1:3:4:6 only at 3 atm., although the product, 5:1:2:4-NH₂·C₆H₂MeCl·SO₃H is dehalogenated at 1 atm. *m*-Toluidine-4-sulphonic acid and 3:4:5:1-OMe·C₆H₂(OH)(NH₂)·CH·N·NH·C(NH)·NH·NO₂, m.p. 223° (decomp.), are described.

R. S. C.

Interaction of OH radicals and of similar free radicals [e.g., NHPH].—See A., 1940, I, 368.

Vicinal substituted resorcinols. I. Alkyl-resorcinols. Synthesis of γ-ethyl-, γ-*n*-propyl-, and γ-*n*-butyl-resorcinol. A. RUSSELL, J. R. FRYE, and W. L. MAULDIN (J. Amer. Chem. Soc., 1940, **62**, 1441—1443).—7-Hydroxy-4-methylcoumarin [prep. from CH₃Ac·CO₂Et and *m*-C₆H₄(OH)₂ in conc. H₂SO₄ at <10°, m.p. 187°, and Ac₂O give the acetate, m.p. 151°, which with AlCl₃ at 125—170° gives 7-hydroxy-8-acetyl-4-methylcoumarin, m.p. 163°. With 12% NaOH in N₂ this yields 2:6:1-(OH)₂·C₆H₃·COMe, m.p. 154—156°, reduced by Zn-Hg-HCl to 2-ethylresorcinol, m.p. 94.5°. Similarly are obtained 7-propionyloxy-, m.p. 148.5°, and 7-*n*-butyryloxy-4-methylcoumarin, m.p. 91°, 7-hydroxy-8-propionyl-, m.p. 187°, and -8-*n*-butyryl-4-methylcoumarin, m.p. 141°, 2:6-dihydroxy-propiophenone, m.p. 133.5°, and -*n*-butyrophenone, m.p. 106°, 2-*n*-propyl-, m.p. 92.5°, and 2-*n*-butyl-resorcinol, m.p. 83°. 7-Hexyloxy-4-methylcoumarin (prep. by *n*-C₅H₁₁·COCl in C₅H₅N), m.p. 72°, does not undergo the Fries rearrangement.

R. S. C.

Structure of cannabidiol. IV. Position of the linking between the two rings. R. ADAMS, H. WOLFF, C. K. KAIN, and J. H. CLARK (J. Amer. Chem. Soc., 1940, **62**, 1770—1775; cf. A., 1940, II, 215).—Absorption spectra and previous evidence indicate that tetrahydrocannabidiol Me₂ ether (I) is probably 2-5'-methyl-2'-isopropylcyclohexyl-5-*n*-amyl-resorcinol. Cannabidiol Me₂ ether, b.p. 168—170°/2 mm., best obtained by boiling MeI-K₂CO₃-COMe₂, with H₂-PtO₂ (2—3 atm.) in AcOH gives (I), b.p. 167—170°/2.5 mm., [α]_D²⁰ -30°. Apparatus for Li reactions is described. LiBu⁴ and *m*-C₆H₄(OMe)₂ give 2:1:3-C₆H₃Li(OMe)₂, which with *l*-menthone (II) gives 1-2':6'-dimethoxyphenyl-5-methyl-2-isopropylcyclohexanol, m.p. 59—60°, [α]_D²⁷ -17°, dehydrated by KHSO₄ at 140—160° to 2-Δ³-3'-menthylresorcinol Me₂ ether, m.p. 88°, b.p. 123—125°/2 mm., [α]_D²⁷ +29°, which with H₂-PtO₂ in AcOH gives 2-3'-menthylresorcinol Me₂ ether (III), m.p. 46°, [α]_D²⁸ -45°. Orcinol Me₂ ether (prep. from orcinol by

NaOMe-Me₂SO₄-MeOH), b.p. 110—112°/7 mm., with LiPh and then (II) gives 1-3':5'-dimethoxy-p-tolyl-5-methyl-2-isopropylcyclohexanol, m.p. 66·5° (uncorr.), [α]_D²⁵ -17°, and thence as above 4-Δ³·3'-menthenyl-, m.p. 103·5—104°, b.p. 132—133°/2 mm., [α]_D²⁵ +40°, and 4-3'-menthyl-*orcinol* Me₂ ether (Me = 1) (IV), m.p. 60—61°, [α]_D²⁵ -36°. The orientation of (IV) is proved by conversion of the Li derivative (prep. by LiBu^a) by CO₂ into 3:5:1:4-(OMe)₂C₆H₃Me·CO₂H. 4:1:3-C₆H₃Br(OMe)₂ gives 4:1:3-C₆H₃Li(OMe)₂ and thence as above 1-2':4'-dimethoxyphenyl-5-methyl-2-isopropylcyclohexanol, b.p. 145—148°/2 mm., [α]_D²⁵ -10·3°, 4-Δ³·3'-menthenyl-, b.p. 140—142°/2 mm., [α]_D²⁵ +52°, and 4-3'-menthyl-*resorcinol*, b.p. 142—145°/2 mm., [α]_D ±0°. *m*-C₆H₄(OH)₂, *l*-menthol, and 85% H₃PO₄ at 140° give 1-4-3'-menthyl-*resorcinol*, b.p. 188—190°/2 mm., [α]_D²⁵ -69°, and thence (NaOMe-Me₂SO₄-MeOH) the 1-Me₂ ether (V), b.p. 143—145°/2 mm., [α]_D²⁵ -5·8°, thereof. *Orcinol* gives similarly 6-3'-menthyl-*orcinol*, b.p. 188—190°/2 mm., [α]_D²⁵ -16°, and its Me₂ ether (VI), b.p. 167—169°/2 mm., [α]_D²⁵ -14·5°. The absorption spectra of (I), (III), and (IV) are very similar but differ from those of (V) and (VI) (a very similar pair). M.p. are corr. unless otherwise stated. [α] are in 95% EtOH. R. S. C.

Valency angle studies. VI. Stability of the tetrahedral angle at a carbon atom. A. LÜTTRINGHAUS and K. BUCHHOLZ. **VII. Relationships between valency angle and isomorphous replacement with bivalent atoms and pseudo-atoms.** A. LÜTTRINGHAUS and K. HAUSCHILD (Ber., 1940, 73, [B], 134—145, 145—153).—It is inferred from experiments on ring-closure by formation of polymethylene ethers that the valency angles about the central C are closely similar in CH₂(C₆H₄·OH)₂ and CMe₂(C₆H₄·OH)₂, showing that the angles are very close to the tetrahedral val. in spite of the large differences in the spatial requirements of the attached groups. The CO valency angle in derivatives of CPh₂ is ≫ the tetrahedral val.; a monomeric polymethylene ether of CO(C₆H₄·OH)₂ is not formed with <(CH₂)₁₂. The increased angle is due to electromeric effects, which tend to equalise the angles between the three units attached to the C; the tendency of the rings to lie in one plane may cause a further increase due to interaction of their H atoms. Previous work is reviewed briefly: distortion of valency angles is due to (a) steric effects of neighbouring substituents (notable with ·O· and ·S·, but very small with ·C·); (b) electromeric effects, as with CO attached to aromatic groups; (c) special effects, such as that resulting from semipolar linkings in ·SO₂ (cf. A., 1940, II, 139), in which two positive charges may occupy valency positions and produce an effectively octahedral configuration at the S atom. The following compounds are prepared by methods described previously (*loc. cit.* and A., 1939, II, 337); ββ-4:4'-dihydroxydiphenylpropane ζ-bromoheptyl ether (I), b.p. 211—215°/0·03 mm., θ-bromo-octyl ether (II), and κ-bromododecyl ether (III), b.p. 230—235°/0·01 mm. Attempted ring-closure (*loc. cit.*) with (I) gives dimeric ββ-4:4'-dihydroxydiphenylpropane hexamethylene ether, m.p. 193·5°; with (II) and (III) intramol. ring-closure gives the octamethylene ether,

CMe₂<C₆H₄·O>[CH₂]₈, m.p. 106°, b.p. 196—200°/0·03 mm. (yield 23·5%), and decamethylene ether, m.p. 60·4° (yield 53·7%), respectively. 4:4'-Dihydroxybenzophenone ζ-bromoheptyl ether, m.p. 104·5° (attempted ring-closure not successful), κ-bromododecyl ether (IV), m.p. 109·5°, and μ-bromododecyl ether (V), m.p. 99°, are similarly prepared; with (IV) ring-closure affords dimeric 4:4'-dihydroxybenzophenone decamethylene ether, m.p. 156°, but the monomeric dodecamethylene ether, m.p. 139°, is obtained from (V) (yield 11·5%).

VII. M.p. diagrams for a no. of binary systems show that CH₂, O, and S are mutually capable of isomorphous replacement when their valency angles are in close agreement, but not otherwise. Thus Ph₂O and CH₂Ph₂ give a simple eutectic system, but fluorene, diphenylene oxide and sulphide, in which distortion of the CH₂, O, and S valency angles is not possible, give complete ranges of mixed crystals. CH₂(C₆H₄·OMe-*p*)₂ and S(C₆H₄·OMe-*p*)₂ have a limited miscibility range in the solid state, but both give simple eutectics with O(C₆H₄·OMe-*p*)₂; this agrees with the observation that CH₂ and S attached to Ph₂ have similar valency angles (~110°) whilst that of O is different (129±4°). Limited miscibility is also

shown by the compounds X<C₆H₄·O>[CH₂]₁₀, where X = CH₂, O, or S; the miscibility gap is again smallest with X = CH₂ and S. 9:9-Dichloro- and 9:9-dimethyl-fluorene also show limited miscibility, indicating that isomorphous replacement is possible with substituents in the 9-positions. A. J. E. W.

Colour reaction of diethylstilbæstrol (4:4'-dihydroxy-αβ-diethylstilbene). E. DINGEMANSE (Nature, 1940, 145, 825).—Addition of several drops of 50% SbCl₅ to a solution of several μg. of stilbæstrol in CHCl₃ produces a fuchsin-red colour; more conc. solutions give a red ppt. On warming, 1 μg. per c.c. of CHCl₃ can be detected. Max. intensity of colour is reached in 15 min. and remains const. for 10—15 min. Fatty and unsaponifiable substances in oily solutions of natural œstrogens must be removed before applying the test. In presence of EtOH the red colour changes rapidly to blue-violet. The reaction has been applied to the colorimetric determination of diethylstilbæstrol in the urine and liver of dogs. L. S. T.

Aminoalkoxydiphenyl derivatives.—See B., 1940, 641.

Acetylenic ethers. I. Phenoxyacetylenes. T. L. JACOBS, R. CRAMER, and F. T. WEISS (J. Amer. Chem. Soc., 1940, 62, 1849—1854).—(CHBr)₂ and KPh in MeOH under defined conditions give 35—45% of CHBr·CH·OPh (I), b.p. 99—100°/8 mm. (Slimmer's method, A., 1903, i, 249, gives 50% yields), the recovered (CHBr)₂ being all *trans*. With KOH powder at 100°/23—25 mm., (I) gives CH·C·OPh (II) (60—80%), m.p. -37° to -36°, b.p. 62—63°/25 mm., and ~12% of PhOH. H₂-PtO₂ reduces (II) to PhOEt. (II) gives a dibromide, m.p. 37—38°, b.p. 127—128°/12 mm., and di-iodide, m.p. 77·5—78·5°. With conc. H₂SO₄ at 0°, (II) gives 80% of phenol-sulphonic acids and AcOH. (II) is stable in solid

CO₂, but polymerises at room temp. (no absorption of O₂; not catalysed by light) and explodes at >100°. The Na derivative (prep. by Na in Et₂O-N₂) with BzCl at 0° gives 65% of PhOBz (held by Slimmer, *loc. cit.*, to be OPh·C:C·OBz). The MgBr derivative of (II) (prep. by MgEtBr in boiling Et₂O) with *p*-C₆H₄Me·SO₃Et (III) gives α -phenoxy- Δ^4 -*n*-butinene (15%), b.p. 98–99°/20 mm., with *p*-C₆H₄Me·SO₃Bu (IV) gives α -phenoxy- Δ^4 -*n*-hexinene (V) (52%), b.p. 122–123°/14 mm., with COMe₂ gives α -phenoxy- γ -methyl- Δ^4 -*n*-butinen- γ -ol (63%), b.p. 91–92°/1 mm., with BzCl or BzBr at –15° gives 38 or 26%, respectively, of PhOBz (and tar), with MeCHO gives α -phenoxy- Δ^4 -*n*-butinen- γ -ol, b.p. 88–89°/1 mm., with CO₂ gives a tar, and with H₂O or CH₂:CH·CH₂Br regenerates 80 and 61%, respectively, of (II); in these reactions a little PhOH is also formed [74% with (III), 20–38% with (IV)]. With H₂-PtO₂, (V) gives *n*-C₆H₁₃·OPh, b.p. 130°/22.5 mm., and with Hg(OAc)₂·HCl·H₂O gives *n*-C₅H₁₁·CO₂Ph. Heating OPh·C:C·MgI in Bu₂O at 90–105° gives 86% of PhOH and a tar. Na in xylene at 90° converts (I) into PhOH (98.1%) and (CHBr)₂ (21%), but Mg in Bu₂O is without effect. The structure of metallic derivatives of (II) is partly analogous to that of allylic derivatives.

R. S. C.

New synthesis of 4:4'-dimethoxy- $\alpha\beta$ -diethylstilbene. E. PÉTERI (J.C.S., 1940, 833–835).—Anisoin and MgEtBr afford $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-*p*-anisylbutane (I), m.p. 114–115° (cf. Weill, A., 1932, 394), oxidised by CrO₃-AcOH at 100° (bath) to anisic acid. Dehydration of (I) with boiling (9 hr.) H₂C₂O₄-AcOH gives >70% of (*p*-OMe·C₆H₄)₂CH·COEt (II), b.p. 210–212°/2 mm., m.p. 56–58°; use of aq. H₂C₂O₄ also affords some (*p*-OMe·C₆H₄)₂CET·CHO (III). $\alpha\alpha$ -Di-*p*-anisylacetonitrile (IV) and MgEtBr give (II), oxidised (CrO₃-AcOH at room temp.) to CO(C₆H₄·OMe-*p*)₂. The oil, b.p. 190–195°/2 mm. [contains (III)], obtained when (I) is boiled for 2 hr., is converted by MgEtBr followed by distillation with a drop of dil. H₂SO₄ into a little [CET(C₆H₄·OMe-*p*)]₂ (V) (cf. Robinson *et al.*, A., 1939, II, 312), obtained similarly from the oily by-product from (I)-H₂C₂O₄-AcOH. *p*-OMe·C₆H₄·CH(OH)·CN, PhOMe, and 73% H₂SO₄ at 80° yield (IV) and thence by 20% KOH-MeOH at 115–120°, $\alpha\alpha$ -di-*p*-anisylacetic acid, m.p. 113–114° [Me (VI), m.p. 71–72°, and Et ester, m.p. 68–69°]. (II) or (VI) (more convenient method) and MgEtBr afford β -hydroxy- $\alpha\alpha$ -di-*p*-anisyl- β -ethylbutane (VII), m.p. 87–88°, dehydrated by distilling with a drop of dil. H₂SO₄ (HCl-EtOH, aq. alkali, ZnCl₂-AcOH, or PCl₅ is less satisfactory) to (*p*-OMe·C₆H₄)₂C:CET₂ (VIII), oxidised, as is (VII), by CrO₃-AcOH at 100° (bath) to CO(C₆H₄·OMe-*p*)₂. (VII) and POCl₃-PhMe give (VIII) and (V). Theoretical aspects of the change (VII) \rightarrow (V) are discussed.

A. T. P.

Hydroxylation of unsaturated substances. VI. Catalytic hydroxylation of cyclopentadiene. N. A. MILAS and L. S. MALONEY (J. Amer. Chem. Soc., 1940, 62, 1841–1843; cf. A., 1939, II, 404).—Cyclopentadiene (0.773), H₂O₂ (0.85 mol.), and a little OsO₄ in BuⁿOH at 0° give (? *cis*-) Δ^4 -cyclopentene-1:3-diol, b.p. 80–83°/1 mm. (*bis*-3:5-dinitrobenzoate,

m.p. 185.5–186°; *CHPh*: derivative, m.p. 115–117°), hydrogenated (PtO₂; EtOH) to (? *cis*-)cyclopentane-1:3-diol, b.p. 120–125°/12 mm. [*di*-*p*-nitrobenzoate, m.p. 179–181°; *di*(phenylurethane), m.p. 168–171°], stable to Pb(OAc)₄. The diol of Dane *et al.* (A., 1937, II, 503) is probably the *trans*-compound. An excess of H₂O₂ yields an amorphous cyclopentane-1:2:3:4-tetraol, discolours at 190–200° (liquid tetrabenzoate).

R. S. C.

Reduction of α -bromo-ketones by aluminium isopropoxide. Isomeric amino-alcohols of the ephedrine series. P. G. STEVENS, O. C. W. ALLENBY, and A. S. DUBOIS (J. Amer. Chem. Soc., 1940, 62, 1424–1428; cf. A., 1939, II, 61).—COPh·CHMeBr (I) and Al(OPr^{*i*})₃ give mixed bromohydrins (A), Pr^{*i*}Br (8%), carbinols [including much CH₂Ph·CHMe·OH (II)], and ? ethers (B). The reactions are: (I) \rightarrow OH·CHPh·CHMeBr (A) \rightarrow α -phenylpropylene $\alpha\beta$ -oxide (III) \rightarrow (Pr^{*i*}OH) OPr^{*i*}·CHPh·CHMe·OH and/or OH·CHPh·CHMe·OPr^{*i*} (B); (III) + AlBr(OPr^{*i*})₂ \rightarrow CH₂Ph·COMe \rightarrow (II). CH₂Ph·CHO and MgMeI give a poor yield of (II) with condensation products, including (?) $\alpha\gamma$ -diphenyl-*n*-pentane- $\beta\delta$ -diol, m.p. 126.5–127° (with CrO₃ gives an oil). NH₂Me and (A) in MeOH give *dl*- ψ -ephedrine and *dl*-isoeephedrine (Emde *et al.*, A., 1911, i, 714; renamed *dl*- ψ -isoeephedrine; hydrochloride, m.p. 188–190.5°). Pure (A) with Al(OPr^{*i*})₃ gives Pr^{*i*}Br and COMe₂ and, later, a mixture containing (II). Al(OPr^{*i*})₃-Pr^{*i*}OH and (III) give mainly an ether (B), b.p. 114–116°/11 mm. (*p*-nitrobenzoate, m.p. 99.5–100°; phenylurethane, m.p. 94.5–95.5°), but in presence of AlBr₃ give much (II). COPh·CMe₂Br (prep. from COPr^{*i*}Br by Br), b.p. 119–120°/10 mm., with boiling Al(OPr^{*i*})₃-Pr^{*i*}OH gives Pr^{*i*}Br (30%), carbinols, C₁₀H₁₄O, b.p. 100–104°/9 mm., and an ether, C₁₃H₂₀O, b.p. 83.8–84.5°/9 mm., but at 33–34°/63–65 mm. gives mainly β -methylcinnamyl bromide, b.p. 115–117°/8 mm. [by way of OH·CHPh·CMe·CH₂ (IV); identified by its physical const. and hydrolysis to β -methylcinnamyl alcohol (V), m.p. 19–21°, b.p. 124–124.3°/8 mm. (dibromide, m.p. 86–87°; phenylurethane, m.p. 78.5–79.3°)]. EtCHO and PhCHO give CHPh·CMe·CHO, b.p. 113°/112 mm. (semicarbazone, m.p. 206–208°), reduced by Al(OPr^{*i*})₃ to (V). CH₂:CMe·CHO and MgPhBr give CH₂:CMe·CHPh·OH, b.p. 99.8–100°/8 mm. (dibromide, an oil; phenylurethane, m.p. 79.5–79.9°), which with HBr followed by hydrolysis (dil. aq. NaOH) yields much (V). 2-Bromocholestanone and Al(OPr^{*i*})₃ give slowly a gum.

R. S. C.

Free radicals and radical stability. IX. Influence of short-lived and long-lived radicals on the reactivity of alcohols. S. T. BOWDEN (J.C.S., 1940, 880–882).—The following alcohols with K in xylene at 100° evolve H₂ at rates \propto the nos. given: CH₂Ph·OH 6.5, CHPh₂·OH 11.2, CPh₃·OH 14.8, *p*-C₆H₄Ph·CPh₂·OH 13.7, 1-C₁₀H₇·CPh₂·OH 9.3. In each case the reaction ceases suddenly before completion. Conductivity measurements in non-polar solvents show that these alcohols are non-ionised.

A. LI.

Kinetics of the reaction of *p*-methoxybenzhydryl chloride with methanol in dilute nitrobenzene solution.—See A., 1940, I, 364.

Free radicals and radical stability. VIII. Stability of formates and reduction of triarylcarbinols. S. T. BOWDEN, D. L. CLARKE, and W. E. HARRIS (J.C.S., 1940, 874—880; cf. A., 1939, II, 156).—Reducibility of $\text{C}_6\text{H}_5\text{O}_2\text{H}$ is examined, with particular reference to thermal stability of formates. Order of resistance to the thermal decomp. $\text{HCO}_2\text{R} \rightarrow \text{RH} + \text{CO}_2$ is $\text{R} = \text{Me}$ (decomp. temp., viz., when CO_2 begins to form, is $>440^\circ$) $> \text{CH}_2\text{Ph}$ (320°) $> \text{CHPh}_2$ (206°) $> \text{CPh}_3$ (49°) $< p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2$ (56°) $< 1\text{-C}_{10}\text{H}_7\cdot\text{CPh}_2$ (68°). Radical stability increases throughout this series, and the inversion of the stability relationships at CPh_3 shows that two different mechanisms are involved, viz., intramol. change in the colourless homopolar formates, and ionic interaction in the coloured polar formates. Decomp. temp. of other formates are: *o*- (I), 48° , *m*-, 49° , and *p*-methoxy-, 48° , 2:2'- (II), 31° , 2:4'-, 42° , and 3:4-dimethoxy-, 47° , 3:4-methylenedioxy-, 48° , 2-methoxy-4'-methyl-, 38° , 3:4:5-, 49° , 2:4:2'-, 44° , 2:2':3'-, 33° , and 3:3':3''-trimethoxy-triphenylmethyl, 120° (formate prepared in xylene), phenyl-*p*-anisylidiphenylmethyl, 50° , and diphenyl-3-acenaphthylmethyl, 120° (in xylene). Apparatus and methods used in varying cases are described. Rates of evolution of CO_2 from solutions of the carbinols in HCO_2H at 77° are measured; apparatus is described. The *o*-OMe promotes decomp. of formate; (I) and (II) give high yields of CHAr_3 . *p*-OMe exerts a fairly strong influence in the CPh_3 series, but the effect is much less with more complex compounds. *m*-OMe appears to exert a slightly favourable influence in early stages of reaction, but soon an inhibitory effect causes low yields of CHAr_3 . Reduction of carbinols with large aryl groups, e.g., $\text{C}_6\text{H}_4\text{Ph}$, C_{10}H_7 , acenaphthyl, is best carried out by Zn-AcOH or HCl-EtOH . ($p\text{-NO}_2\cdot\text{C}_6\text{H}_4$) $_3\text{C}\cdot\text{OH}$ dissolves in HCO_2H to a colourless solution which does not evolve CO_2 at 100° . Experimental and theoretical evidence suggests that there is no simple connexion between the basicity of a carbinol and its reducibility as indicated by the HCO_2H method. *o*-OMe- $\text{C}_6\text{H}_4\cdot\text{MgI}$ (III) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COPh}$ (improved prep.) give 2-methoxy-4'-methyltriphenylcarbinol, m.p. 126° . 2:4:1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{COPh}$ and (III) afford 2:4:2'-trimethoxy-triphenylcarbinol, m.p. $119\text{--}120^\circ$ (triphenylmethane, m.p. 118°). $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{MgBr}$ and COPh_2 give $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2\cdot\text{OH}$, m.p. 136° (cf. A., 1931, 1406), $1\text{-C}_{10}\text{H}_7\cdot\text{COPh}$ and MgPhBr afford $1\text{-C}_{10}\text{H}_7\cdot\text{CPh}_2\cdot\text{OH}$, m.p. 135° . A. T. P.

Brassicasterol, the characteristic sterol of rapeseed oil. E. FERNHOLZ and H. E. STAVELY (J. Amer. Chem. Soc., 1940, 62, 1875—1877).—Ozonisation of brassicasteryl acetate dibromide gives $\text{CHMePr}^6\cdot\text{CHO}$ and, after debromination, β -3-acetoxibisnorcholenic acid. Hydrogenation of brassicasterol (I) gives ergosterol. (I) is, therefore, 7:8-dihydro-ergosterol. It has m.p. 148° and gives an acetate, m.p. 158° (tetrabromide, m.p. $205\text{--}213^\circ$), propionate, m.p. 132° , and benzoate, m.p. 167° . No details are given. R. S. C.

Elimination of hydrogen bromide from stigmasterol 22:23-dibromide. E. FERNHOLZ, W. L. RUGH, and H. E. STAVELY (J. Amer. Chem. Soc.,

1940, 62, 1554—1556).—Stigmasteryl acetate 22:23-dibromide with boiling 20% KOH-EtOH or $\text{C}_5\text{H}_5\text{N}$ or quinoline gives stigmasterol or its acetate, but with KOAc in boiling $\text{CH}_3\text{EtBu}^n\cdot\text{CH}_2\cdot\text{OH}$ in presence of a little quinol gives $\Delta^5:22:24\text{--}28\text{-stigmatrien-3-yl acetate}$ (I), m.p. $128\text{--}129^\circ$ (in CO_2), $[\alpha]_D^{24} -47^\circ$ in CHCl_3 [absorption max. 2375 Å. (ϵ 17,000)], which adds $(\text{CH}\cdot\text{CO})_2\text{O}$ (product not purified), resists reduction by Na-EtOH , but, when hydrogenated (3 H_2 ; PtO_2 ; AcOH), yields stigmastyl acetate, and with O_3 gives MeCHO (isolated chromatographically as $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CHMe}$). Hot 0.5N- KOH-95\% EtOH hydrolyses (I) to the alcohol, m.p. $125\text{--}126^\circ$ (in CO_2). Autoxidation of (I) to a peroxide is rapid. The structure of (I) follows from the reactions described. R. S. C.

2:4-Dibromo- α -cestradiol. R. B. WOODWARD (J. Amer. Chem. Soc., 1940, 62, 1625—1626).— α -Cestradiol and NHAcBr in abs. EtOH at room temp. give the 2:4- Br_2 -derivative, m.p. $215.5\text{--}216.5^\circ$ (corr.), stable to AgNO_3 - or KOH-EtOH . R. S. C.

Preparation of cholestanyl glucosides with all four possible configurations of the glucoside linking. R. P. LINSTAD (J. Amer. Chem. Soc., 1940, 62, 1766—1770).—Contrary to Miescher *et al.* (A., 1938, II, 174; cf. Gillespie *et al.*, A., 1940, II, 119), no connexion exists between ease of glucoside formation and configuration of cyclic alcohols. Cholesterol (I), bromoglucose tetra-acetate (II), and $\text{Hg}(\text{OAc})_2$ in boiling C_6H_6 give 40% of cholestanyl- α -glucoside tetra-acetate, m.p. $183.5\text{--}184^\circ$, $[\alpha]_D^{25} +114^\circ$ in CHCl_3 , hydrolysed by 0.2N- $\text{Ba}(\text{OH})_2$ in EtOH at room temp. to cholestanyl- α -glucoside, m.p. $\sim 253^\circ$ (decomp.), $[\alpha]_D^{28.7} +94^\circ$ in $\text{C}_5\text{H}_5\text{N}$ [hydrolysed by boiling HCl to (I) and glucose]. With Ag_2O , CaSO_4 , and I in CHCl_3 , (I) and (II) give cholestanyl- β -glucoside tetra-acetate (56%), m.p. 175° , $[\alpha]_D^{24.7} +5^\circ$ in CHCl_3 , and thence cholestanyl- β -glucoside, m.p. $\sim 270^\circ$ (decomp. from 240°), $[\alpha]_D^{24.4} -17^\circ$ in $\text{C}_5\text{H}_5\text{N}$. *epi*Cholestanyl- α -, m.p. 219° , $[\alpha]_D^{26.5} +106^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (tetra-, m.p. 130° , $[\alpha]_D^{24.8} +92.5^\circ$ in CHCl_3 , and tri-acetate, m.p. $86\text{--}88^\circ$ after softening), and - β -glucoside, m.p. $216\text{--}217^\circ$, $[\alpha]_D^{26.7} +1^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (tetra-acetate, m.p. 173° , $[\alpha]_D^{27.2} -3^\circ$ in CHCl_3), are similarly prepared, but must be reacylated before isolation as tetra-acetates. *epi*Cholesterol can be separated from (I) by the much greater solubility of the glucosides of the former in org. solvents. M.p. are corr.

R. S. C.

Optically active α -carbomethoxy- α - γ -diphenyl- γ -naphthylallene. E. P. KOHLER and W. J. WHITCHER (J. Amer. Chem. Soc., 1940, 62, 1489—1490).—*dl*- α - $\text{C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{C}\cdot\text{CPh}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) and CH_2N_2 give the *dl*-Me ester, m.p. 113° , but the *l*-acid gives oils. *Me* 1- α -diphenyl- γ -1-naphthylallene- α -carboxylate, m.p. 91° , $[\alpha]_D -49.8^\circ$ in C_6H_6 , is obtained from the *l*-acid by CH_2N_2 or by treating the *l*-Ag salt with MeI , and the *d*-ester (II), m.p. 91° , $[\alpha]_D +49.3^\circ$ in C_6H_6 , is prepared from the *d*-form of (I) by MeOH-KOH . A trace of HBr in C_6H_6 converts (II) into α - γ -diphenyl- γ -1-naphthyl- γ -crotonolactone. The active esters are stable in C_6H_6 or EtOAc in the dark, but in light are racemised and partly resinified. R. S. C.

Chaulmoogric acid series. II. Synthesis of Δ^2 -cyclopentenecarboxylic acid. K. V. BOKIL and K. S. NARGUND (Proc. Indian Acad. Sci., 1940, 11, A, 409—412).—Et 2-hydroxycyclopentane-1-carboxylate is dehydrated (P_2O_5 in C_6H_6 at 100°) to a mixture of esters hydrolysed by cold KOH-MeOH to an acid mixture from which Δ^1 -cyclopentenecarboxylic acid, m.p. 123 — 124° (anilide, m.p. 126° ; p-toluidide, m.p. 122°), separates. Repeated esterification and hydrolysis of the liquid remainder leads to the isolation of Et Δ^2 -cyclopentenecarboxylate, b.p. $62^\circ/10$ mm., hydrolysed to the acid [γ -aleprolic acid], b.p. 97 — $98^\circ/7$ mm. (anilide, m.p. 134 — 135° ; p-toluidide, m.p. 126 — 127°). The low I vals. of these compounds are due to the instability of the I additive product.

H. W.

Organic derivatives of sulphur, selenium, and tellurium. I. D. T. LEWIS (J.C.S., 1940, 831—832).—The C_6H_5N -BzCl adduct (I) (cf. Dehn *et al.*, A., 1914, i, 1169) and H_2S afford BzSH and dithiobenzoyl oxide, $(CSPH_2)_2O$ (II), m.p. 112° ; (II) and 50% HNO_3 give a small amount of dibenzoyl disulphone, m.p. 141° . (II)-KOH-EtOH, then HCl, afford H_2S , BzOH, and BzSH. With conc. HNO_3 or NH_2Ph (excess), (II) gives BzOH or $NHPhBz$, respectively. (I) and H_2Se yield BzSeH, m.p. 132 — 133° , but BzTeH could not be prepared similarly. CCl_3 -CHO and H_2S - Et_2O , or better, CCl_3 -CH(OH) $_2$ (III) and H_2S -aq. HCl, afford $[CCl_3\cdot CH(OH)]_2S$, m.p. 128° (cf. Hagemann, A., 1872, 494). (III) and H_2Se -HCl (excess) yield bis-($\beta\beta\beta$ -trichloro- α -hydroxyethyl) selenide, m.p. 94 — 98° (decomp. into CCl_3 -CHO + H_2Se).

A. T. P.

Condensations brought about by bases. X. Michael type of condensation with esters and $\alpha\beta$ -unsaturated keto-compounds. C. R. HAUSER and B. ABRAMOVITCH (J. Amer. Chem. Soc., 1940, 62, 1763—1766; cf. A., 1940, II, 171).—EtOAc, which with CPh_3Na very rapidly gives $CH_2Ac\cdot CO_2Et$ (I), condenses with $CHPh\cdot CH\cdot CPh$ and CPh_3Na in Et_2O to give $CO_2Et\cdot CHAc\cdot CHPh\cdot CH_2\cdot CPh$, doubtless by way of (I). Pr^iCO_2Et , which undergoes Claisen condensation only slowly, suffers only Michael condensation with $CHPh\cdot CH\cdot CO_2Et$ (II) in presence of NaOEt or CPh_3Na to give Et $_2$ β -phenyl- α -dimethylglutarate, b.p. 174 — $175^\circ/8$ mm. (corresponding acid, softens at 165° , m.p. 171 — 172.5°). $CH_2Ph\cdot CO_2Et$, (II), and CPh_3Na in Et_2O give Et $_2$ $\alpha\beta$ -diphenylglutarate, m.p. 75 — 75.5° [derived acid, m.p. 196.5 — 197.5° or 207.5 — 218.5° (decomp.) according to the solvent used]. Temp. are corr.

R. S. C.

β -Benzhydrylglutaric acid. M. S. NEWMAN, L. M. JOSHEL, and P. H. WISE (J. Amer. Chem. Soc., 1940, 62, 1861—1863).— $CPh_2\cdot CH\cdot CH_2\cdot CO_2Et$ and $CHNa(CO_2Et)_2$ in boiling EtOH give an ester, converted by hydrolysis and decarboxylation into $CHPh_2\cdot CH(CH_2\cdot CO_2H)_2$ (I) (8.9%), m.p. 176 — 177° , best obtained by the method of Newman *et al.* (A., 1938, II, 132). $CPh_2\cdot CH\cdot CH_2\cdot CO_2H$ and Br give β -bromo- $\gamma\gamma$ -diphenyl- γ -butyrolactone, m.p. 130.6 — 131.2° , converted by boiling C_5H_5N into $\gamma\gamma$ -diphenyl- γ -crotonolactone, m.p. 131.6 — 132.2° , which with $CHNa(CO_2Et)_2$ in boiling Et_2O - C_6H_6 gives an ester, whence hydrolysis by boiling H_2SO_4 -AcOH- H_2O and

subsequent decarboxylation at 250° yields 44—45% of $\gamma\gamma$ -diphenyl- β -carboxymethyl- γ -butyrolactone, m.p. 182.8 — 183.8° , unaffected by Zn-Hg-HCl, Zn dust-alkali, or HI-AcOH. The Grignard reagent, prepared from cyclopentadiene by $MgEtBr$ in Et_2O - C_6H_6 , with $CHPh_2Br$ gives 41% of (?) benzhydrylidene-cyclopentene, m.p. 25 — 30° , b.p. 163 — $165^\circ/4$ mm., ozonised to $COPH_2$ (79%). $CHPh_2\cdot CHO$ and PCl_5 in C_6H_6 give meso- and dl-($CHPhCl$) $_2$. M.p. are corr.

R. S. C.

Reactivities of dienes, especially toward maleic anhydride. II. F. BERGMANN and E. BERGMANN (J. Amer. Chem. Soc., 1940, 62, 1699—1704; cf. A., 1937, II, 407).—Presence of aryl residues on three, but not two, neighbouring C of C:C:C:C (one C:C may be part of a ring) prevents addition of $(:CH\cdot CO)_2O$ (I). The 9:10-ethylenic linking of 9-alkenylphenanthrenes sometimes behaves as part of an aliphatic system and sometimes has aromatic character. 1- α -Naphthyl- Δ^1 -cyclohexene (picrate, new m.p. 129°) does not react (cf. Bachmann *et al.*, A., 1938, II, 443) with an excess of (I) at 110° . However, 1- β -naphthyl- Δ^1 -cyclohexene (prep. by condensing cyclohexanone with 2- $C_{10}H_7$ -MgBr and dehydrating the product by $KHSO_4$ at 150 — 160°), m.p. 61 — 62° , b.p. $144^\circ/2$ mm. (picrate, m.p. 78°), with (I) (excess) at 100° gives 1a:1:2:2a:3:4:5:6-octahydrochrysene-1:2-di-carboxylic anhydride, m.p. 216° , but with p-O: C_6H_4 :O gives a hydrocarbon, $C_{22}H_{16}$, m.p. 178° . 2-isopropenylantracene (prep. from 2-acetylanthracene by $MgMeI$ in boiling Et_2O - C_6H_6), m.p. 154° , and (I) in boiling C_6H_6 give the 9:10-endo- $\alpha\beta$ -succinic anhydride, m.p. 266° . Mg 9-phenanthryl bromide and $COPH\cdot CH_2Ph$ in boiling C_6H_6 give $\alpha\beta$ -diphenyl- α -9-phenanthrylethyl alcohol, m.p. 191 — 192° , dehydrated by $KHSO_4$ at 180 — 190° to α -9-phenanthrylstilbene, m.p. 162° , which gives no picrate or adduct with (I). β -9-Phenanthrylstyrene (II) and Br- CCl_4 at 5° give the dibromide, m.p. 184 — 185° (decomp.), converted by 10% KOH-MeOH at 150° into 9-phenylacetylphenanthrene, m.p. 136° , which is obtained also from β -phenyl- α -9-phenanthrylethyl alcohol by CrO_3 -AcOH first at room temp. and later at 100° . 9-Cyano-phenanthrene and $CH_2Ph\cdot MgCl$ (III) give 9-phenanthryl CH_2Ph ketimine, m.p. 195° , resistant to hydrolysis by HCl-COMe $_2$ - H_2O or conc. HCl at 150° . Attempts to cyclise (II) or 9-propenylphenanthrene (IV) by $AlCl_3$ gave phenanthrene and resin; 9-allyl phenanthrene (V) gives a substance, $(C_{17}H_{14})_n$, m.p. 264° . Li in Et_2O causes dimerisation of (IV), giving, after hydrolysis, ? $\alpha\delta$ -di-9-phenanthryl- $\beta\gamma$ -dimethyl-n-butane, m.p. 222° , b.p. 300 — $310^\circ/0.8$ mm. Li and (V) in Et_2O give the α -Li derivative, since hydrolysis by EtOH regenerates (V) (some 9:10-cyclopentenophenanthrene is also formed by isomerisation) and interaction with PhCHO (2 mols.) gives α -phenyl- β -9-phenanthryl- Δ^2 -buten- α -ol, b.p. 250 — $260^\circ/1.5$ mm. $CHPh\cdot CPh\cdot CH\cdot CHMe$ (VI), b.p. 138 — $140^\circ/1.5$ mm. (no picrate isolable), with (I) in boiling xylene gives 3:4-diphenyl-6-methyl-1:2:3:6-tetrahydrophthalic anhydride, m.p. 168 — 169° . 3:4-Diphenyl-6-methyl-phthalic anhydride, m.p. 161° , is obtained in $PhNO_2$ and with $AlCl_3$ in hot C_6H_6 gives 4-phenyl-2-methyl-fluorenone-1-carboxylic acid, m.p. 196° . 2 Li add to (VI) in Et_2O , hydrolysis of the product giving $\alpha\beta$ -di-

phenyl-Δ^β- or *-Δ^γ-n-pentene*, b.p. 120°/0.4 mm., and a small amount of a fraction, b.p. 190—200°/0.02 mm. *CHPh·CPh·CHO* and (III) in *C₆H₆* give a product, converted by boiling *Ac₂O* into *αβδ-triphenyl-Δ^{αγ}-butadiene*, forms, m.p. 110° (lit. 104—105°), and a liquid (unstable red, cryst. picrate); the latter form with (I) in boiling xylene gives 3:4:6-*triphenyl-1:2:3:6-tetrahydrophthalic anhydride*, m.p. 208—209°; the mixture adds 2 Li, giving after hydrolysis *αβδ-triphenyl-Δ^α*- or *-Δ^β-n-butene*, b.p. 140°/0.3 mm.

R. S. C.

Direct synthesis of resolvable diaryls. E. R. ATKINSON and H. J. LAWLER (J. Amer. Chem. Soc., 1940, 62, 1704—1708).—2:3:5:1-NH₂·C₆H₃Cl₂·CO₂H (I) [prep. from *o*-NH₂·C₆H₄·CO₂H by SO₂Cl₂-C₆H₆ (51%) or Cl₂-AcOH (57%)], when diazotised and then added to Cu₂O in aq. NH₃ gives dl-4:6:4':6'-*tetrachlorodiphenic acid* (49%), m.p. 258—259°, some (I) being regenerated. Resolution by brucine gives l-, m.p. 240—256°, [α]_D²⁵ -129° in CHCl₃ (*brucine salt*, m.p. 264—265°, [α]_D²⁴ -26.5° in CHCl₃), and d-4:6:4':6'-*tetrachlorodiphenic acid*, m.p. 252—254°, [α]_D²⁵ +133° in CHCl₃ [*brucine*, m.p. 254—259°, [α]_D²⁴ -7.9°, and *brucine H salt*, m.p. 263—265° (decomp.), [α]_D²⁵ -15.3° in CHCl₃]. 2:3:5:1-NH₂·C₆H₃Br₂·CO₂H, m.p. 232—233°, gives similarly dl- (37%), m.p. 305—308°, l-, m.p. 282—283°, [α]_D²⁵ -7.7° in abs. EtOH [*brucine salt*, m.p. 259—260° (decomp.), [α]_D²⁴ -10.6° in CHCl₃], and d-4:6:4':6'-*tetrabromodiphenic acid*, m.p. 279—282°, [α]_D²⁵ +6.7° in abs. EtOH [*brucine salt*, m.p. 123—204° (decomp.), [α]_D²⁵ -32.2° in CHCl₃]. The active acids are stable in boiling N-NaOH (cf. Yuan *et al.*, A., 1935, 1237).

R. S. C.

7-Cholanthroic acid. L. F. FIESER and G. W. KILMER (J. Amer. Chem. Soc., 1940, 62, 1354—1360).—Acenaphthene (I) and CH₂Ph·CO₂H in HF give 30% of 3-, m.p. 113.5—114° (unstable picrate, m.p. 107.5—108.5°; oxidised by NaOI in dioxan to 3-acenaphthoic acid), and a little 1-*phenylacetoacenaphthene*, m.p. 81—81.5° (isolated as dimorphic picrate, m.p. 133—134°; oxidised to 1-acenaphthoic acid). *o*-C₆H₄Br·COCl and CH₂N₂ in Et₂O at 0° give *o*-C₆H₄Br·CO·CHN₂, m.p. 42—43° (gas), and thence (Ag₂O-Na₂S₂O₃-H₂O; 60—65°) *o*-C₆H₄Br·CH₂·CO₂H, which with (I) in HF gives a difficultly separable mixture of *o*-bromophenylacetoacenaphthenes, m.p. 128—129.5° and 122—123° (110.5—112.5°). 1-Acenaphthoyl chloride gives similarly the CHN₂ ketone, m.p. 141—142° (decomp.), and 1-acenaphthylacetic acid (II) (63.5%), m.p. 163.5—164.4°. 1-Acetoacenaphthene (modified prep.) and yellow NH₄HS in dioxan at 160° give, on a small scale, an amide, whence boiling 15% NaOH yields 57% of (II), but in large-scale experiments at 175—180° only 36.8% of (II) with 46.7% (65% at 170°, 43% at 188—190°) of 1-ethylacenaphthene, m.p. 34.8—35.1° (lit. 30°), b.p. 160—163°/6 mm. [picrate, m.p. 104.7—105.1° (lit. 102—102.5°)]. COPhBu^δ gives similarly 1.8% of Ph·[CH₂]₂·CHMe·CO·NH₂ (Willgerodt *et al.*, A., 1909, i, 716, state 14—15%). K 1-acenaphthylacetate (II) and *o*-C₆H₄Cl·CHO with a drop of C₅H₅N in Ac₂O at 180° give 55% of *o*-chloro-*α*-1-acenaphthylcinnamic acid, m.p. 221.5—223.5° after softening, which with KOH at 254° or in boiling quino-

line gives tars. *o*-NO₂·C₆H₄·CHO and (II) in Ac₂O at 125—130° give *o*-nitro-, m.p. 244.5—244.9° (decomp.), reduced by FeSO₄-NH₃-H₂O to *o*-amino-*α*-1-acenaphthylcinnamic acid, m.p. 229—230.5° (227—229°), obtained less well by H₂-PtO₂-EtOH with substances, m.p. 236.4—238.4° (decomp.) or (III) 278—279.5°. Diazotisation (*iso*-C₅H₁₁·O·NO in EtOH-dioxan-H₂SO₄) and treatment with Cu gives a gummy acid, the Me ester of which by chromatography yields *Me 7-methylcholanthroate* (4.5%), m.p. 159—159.2° (absorption spectrum resembles that of cholanthrene) [with a substance (? III), m.p. 280.3—281.2° (decomp.)], and thence by 10% KOH-EtOH 7-cholanthroic acid, decomp. 258.5—261° (sublimes from 255°). Decarboxylation of this acid is difficult, but heating the crude product of ring-closure with basic Cu carbonate at 300°/vac. gives 8.1% of cholanthene. M.p. arc corr.

R. S. C.

Δ⁵-3(*t*):17-Dihydroxyætiocolenamamide, m.p. 295—296°, and **Δ⁵:16-3(*t*)-hydroxyætiocoladienamamide**, m.p. 254—258°.—See B., 1940, 641.

isoDihydroxycholenic acid. Specificity of Hammersten's reaction for cholic acid. K. YAMASAKI, K. TAKAHASHI, and C. H. KIM (J. Biochem. Japan, 1939, 30, 239—246).—The Hammersten reaction is positive with bile acids with *sec.* OH at C₇ and C₁₂, and CO at C₃; acids without *sec.* or CO groups at C₃ do not give the reaction. *apo*Cholic acid with ZnCl₂-AcOH yields dihydroxycholenic acid (I) and isodihydroxycholenic acid (II). (II) is also given by (I) and ZnCl₂ and by cholic acid and ZnCl₂, FeCl₃, or SbCl₃ (cf. A., 1933, 1162).

F. O. H.

Benzylidene-2:4:6-tribromoaniline. W. S. EMERSON and F. C. UHLE (J. Amer. Chem. Soc., 1940, 62, 1880).—This substance, m.p. 94—95°, is prepared.

R. S. C.

Action of hexamethylenetetramine on the methyl esters of phenolcarboxylic acids. I. Synthesis of 2:4-dihydroxy-5-formylbenzoic acid. R. D. DESAI and K. S. RADHA (Proc. Indian Acad. Sci., 1940, 11, A, 422—423).—2:4-Dihydroxy-5-formylbenzoic acid, m.p. 185—186° (*semicarbazone*, m.p. >290°; *p*-nitro-, m.p. >280°, and 2:4-dinitro-, m.p. >280°, -*phenylhydrazine*), is obtained when anhyd. Me β-resorcyate and (CH₂)₆N₄ react in boiling AcOH to which aq. HCl (1:1) is subsequently added.

H. W.

Preparation of phenylacetone. J. P. MASON and L. I. TERRY (J. Amer. Chem. Soc., 1940, 62, 1622).—COMe·CH₂Ph is obtained in 32% yield from COMe·CH₂Cl, C₆H₆, and AlCl₃ at 100° (bath).

R. S. C.

Condensation of α-methoxystyrene with halogen compounds. C. W. MORTENSON and M. A. SPIELMAN (J. Amer. Chem. Soc., 1940, 62, 1609—1610).—OMe·CPh·CH₂ (I) with CH₂PhBr at 220° gives Ph·[CH₂]₂·COPh (51% with an excess of CH₂PhBr, 35% with 1 mol.) and MeBr (identified by methylation of saccharin), with Bu^δBr at 245° gives COPh·C₅H_{11-n} (28%), with CH₂Cl·CO₂Et at 200° gives COPh·[CH₂]₂·CO₂Et (36%), COPhMe, and *s*-C₆H₃Ph₃ (II), and with BzCl at 180° gives CHBz₃, but with an excess of BzCl gives only (II). PhBr

does not react with (I). The (II) arises by action of HCl on (I) (proved experimentally). These and other condensations (A., 1934, 190; 1939, II, 216) of (I) are analogous to conversion of $\text{NEt}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ by MeI into $\text{I}\{\text{NEt}_2\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$. R. S. C.

$\alpha\beta$ -Unsaturated α - and β -dialkylamino-ketones. N. H. CROMWELL (J. Amer. Chem. Soc., 1940, 62, 1672—1673).— $\text{CMe}\cdot\text{CH}_2\cdot\text{COPh}$, NHEt_2 (2 mols.), and a drop of conc. HCl at 110° give γ -diethylamino- α -phenyl- Δ^8 -buten- α -one, m.p. 70 — 71° . $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COPh}$ and NHEt_2 (3 mols.) in EtOH at room temp. give *Ph* α -diethylaminostyryl ketone, m.p. 51 — 53° (hydrochloride, m.p. 106 — 110°), hydrolysed by 15% H_2SO_4 at 100° to $\text{COPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. CH_2Bz_2 , NHEt_2 (2 mols.), and a drop of HCl at 150° give a poor yield of $\text{COPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{NEt}_2$, m.p. 61 — 62° . R. S. C.

Fries rearrangement of phenyl laurate and stearate. H. E. BELL and J. E. DRIVER (J.C.S., 1940, 835—837).—Ph laurate and AlCl_3 at 150° afford *o*-, m.p. 43.8 — 44.6° (2:4-dinitrophenylhydrazone, m.p. 89 — 89.2°), and (mainly) *p*-hydroxyphenyl undecyl ketone, m.p. 70.5 — 71° , b.p. $277^\circ/15$ mm. (benzoate, m.p. 109 — 109.8° ; semicarbazone, m.p. 143 — 143.6° ; 2:4-dinitrophenylhydrazone, m.p. 151 — 151.2°); the latter is reduced (Clemmensen) to *p*-dodecylphenol, m.p. 65.5 — 66° . Similarly prepared are *o*-, m.p. 66 — 67° (2:4-dinitrophenylhydrazone, m.p. 97.4 — 97.8°), and *p*-hydroxyphenyl heptadecyl ketone, m.p. 90 — 90.5° , b.p. $320^\circ/15$ mm. (benzoate, m.p. 113.2 — 113.6° ; semicarbazone, m.p. 133.4 — 134.7° ; 2:4-dinitrophenylhydrazone, m.p. 142 — 142.2° ; *p*-octadecylphenol, m.p. 83 — 84°). A. T. P.

Action of Grignard reagents on methyl *r*-tropate and atropate. A. MCKENZIE and E. R. WINTON (J.C.S., 1940, 840—844).—Me *r*-tropate (I), m.p. 36 — 37.5° and MgPhBr give *r*-benzyldeoxybenzoin [Ph $\alpha\beta$ -diphenylethyl ketone] (II), m.p. 120 — 121° (2:4-dinitrophenylhydrazone, m.p. 163 — 164°), converted by MgPhBr into *r*- α -hydroxy- $\alpha\beta\gamma$ -tetraphenylpropane, m.p. 146 — 147° . Me (—)-tropate, b.p. 157 — $159^\circ/16$ mm., $[\alpha]_{546}^{20} -54.1^\circ$ in CMe_2 , and MgPhBr also afford (II). Me (+)-tropate has b.p. 162 — $163^\circ/20$ mm., $[\alpha]_{546}^{20} +83.3^\circ$ in CMe_2 . MgMeI and (I) give *dl*- γ -phenylpentan- β -one (III) [semicarbazone (IV), new m.p. 195 — 196° ; *dl*- $\text{COEt}\cdot\text{CHPh}\cdot\text{OH}$ and MgMeI give *r*- $\alpha\beta$ -dihydroxy- α -phenyl- β -methylbutane, m.p. 71 — 72° , converted by conc. H_2SO_4 at room temp. into (III) and thence (IV)] and (mainly) *r*- $\alpha\gamma$ -dihydroxy- β -phenyl- γ -methylbutane (V), m.p. 80 — 81° (unchanged by distilling in high vac.). (V)— MgMeI — Et_2O give (III). (V) and boiling dil. H_2SO_4 yield an oil which affords no semicarbazone or dinitrophenylhydrazone. Me atropate, b.p. 106 — $109^\circ/12$ mm., with MgPhBr or MgMeI gives (II) or (III), respectively. Mechanisms of reactions are discussed. *r*-Tropic acid does not react with MgPhBr at room temp. A. T. P.

Ring-enlargement of two cyclic α -chloro-ketones. T. R. STEADMAN (J. Amer. Chem. Soc., 1940, 62, 1606—1609).—2-Chlorocyclohexanone (I), $\text{NO}\cdot\text{NMe}\cdot\text{CO}_2\text{Et}$ (1.1 mol.), and a little Na_2CO_3 in abs. MeOH at 20 — 30° give 52% of 2-chlorocyclo-

heptanone (I), b.p. 87 — $88^\circ/10$ mm. (with boiling KOH — EtOH gives 36% of hexahydrobenzoic acid), and 16% of 2-chloro-1-methylenecyclohexane oxide, $[\text{CH}_2]_4\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix} \text{CH}_2$, m.p. -10° to -8° , b.p. 62 — $63^\circ/10$ mm. (converted by H_2 —Raney Ni in 95% EtOH into cyclohexylcarbinol, identified as phenylurethane). (I) gives similarly 13% of 2-chlorocyclooctanone (II) and 11.7% of 2-chloro-1-methylenecycloheptane oxide, b.p. 84 — $86^\circ/10$ mm. (with NaOH — EtOH gives cycloheptanecarboxylic acid), 38% of (I) being recovered. When kept in air, (II) gives some suberic acid.

R. S. C.

Sterol- α estrone group. II. Derivatives of 2-phenylcyclohexanone. J. C. BARDHAN (J.C.S., 1940, 848—850).—Partly an account of work previously reviewed (A., 1940, II, 253). *Et* δ -keto- α -cyano- α -phenylhexoate, b.p. $186^\circ/16$ mm., and *Et* β -2-keto-6-carbethoxy-3-phenyl-6-methylcyclohexylpropionate, b.p. $200^\circ/5$ mm., are described. *Et* δ -keto- α -carbethoxy- α -phenylhexoate and the compounds derived from it (*loc. cit.*) are new.

A. T. P.

Preparation of 1-keto-3-methyl-1:2:3:4-tetrahydronaphthalene and β -3-methyl-1:2:3:4-tetrahydro-1-naphthylethyl alcohol. W. E. BACHMANN and W. S. STRUVE (J. Amer. Chem. Soc., 1940, 62, 1618—1619).— $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COCl}$ (prepared from the acid by SOCl_2 and a little $\text{C}_5\text{H}_5\text{N}$) and AlCl_3 in CS_2 at $<0^\circ$ and then at the b.p. give 73% of 1-keto-3-methyl-1:2:3:4-tetrahydronaphthalene (I), b.p. 94 — $96^\circ/0.3$ mm. (oxime, m.p. 122.5 — 123.5°), which by Clemmensen reduction, followed by heating at 200 — 220° , first with S and then with S and Cu-bronze, gives $2\cdot\text{C}_{10}\text{H}_7\cdot\text{Me}$. With $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$, Zn, and a trace of I in Et_2O — C_6H_6 , (I) gives a OH-ester, dehydrated by anhyd. HCO_2H to Me 3-methyl-(? 3:4)-dihydro-1-naphthylacetate (85%), b.p. 130 — $133^\circ/0.4$ mm., which with Na—MeOH yields β -3-methyl-1:2:3:4-tetrahydro-1-naphthylethyl alcohol (57%), b.p. 134 — $137^\circ/0.4$ mm., and thence (PBr_3 ; 100°) the bromide (75%), b.p. 137 — $140^\circ/0.4$ mm. R. S. C.

Benzantrones. F. G. BADDAR (Nature, 1940, 145, 822; cf. A., 1938, II, 236).—Ring-closure (conc. H_2SO_4 ; PCl_5 + AlCl_3 ; P_2O_5) of *o*- α -naphthylbenzoic acid at different temp. gives mesobenzanthrone and 3:4-benzfluorenone (cf. Grieve *et al.*, A., 1938, II, 93). Cyclisation of *o*-4'-methyl-1'-naphthylbenzoic acid gives a mixture of 1'-methylmesobenzanthrone and 2-methyl-3:4-benzfluorenone. Condensation of diazotised *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ with 1- and $2\cdot\text{C}_{10}\text{H}_7\cdot\text{Me}$ at 25° gives a mixture of acids, and *o*-2'-methyl-1'-naphthylbenzoic acid, respectively. L. S. T.

Steroid ketones.—See B., 1940, 641.

Treatment of 2-bromocholestanone with collidine. R. P. JACOBSEN (J. Amer. Chem. Soc., 1940, 62, 1620—1621).—HBr is only partly removed from 2-bromocholestanone by boiling collidine, the products being cholestanone and Δ^1 -cholestenone (I), $+\text{H}_2\text{O}$, m.p. 107 — 108° , $[\alpha]_{\text{D}}^{25} +65^\circ$ [isolated as dibromide, decomp. 85° , which with NaI or Zn dust in EtOH or KI in 80% CMe_2 gives (I)]. The absorption spectra of (I) (max. 2320 \AA ; $\log \epsilon 4.0$) and Δ^4 -cholestenone (max. 2400 \AA ; $\log \epsilon 4.27$) are reported. R. S. C.

Molecular species in aqueous quinhydrone solutions. C. WAGNER and K. GRÜNEWALD (Z. Elektrochem., 1940, 46, 265—269).—From measurements of the dependence of light absorption on concn., the quinhydrone solutions contain meriquinone mols., $C_6H_4O_2$, $C_6H_4(OH)_2$; semiquinone radicals, $C_6H_4O(OH)$, are not detectable. F. J. G.

Vitamin-K activity of quinones. E. FERNHOLZ, H. B. MACPHILLAMY, and S. ANSBACHER (J. Amer. Chem. Soc., 1940, 62, 1619—1620).—Min. active doses are 2-methyl-5:6:7:8-tetrahydro-1:4-naphthaquinone, m.p. 58—59° [prep. from 2-methyl-1:4-naphthaquinone (I) by H_2 -PtO₂ in AcOH, followed by FeCl₃-oxidation], 1 mg., $\beta\gamma$:5:6:7:8-hexahydrovitamin-K₁ (similarly prepared; an oil) >2 mg., naphthotocopherol (II) [prep. from (I) by phytol and ZnCl₂ in xylene] >1 mg., and the oily product, $C_{31}H_{48}O_3$, obtained from (II) by FeCl₃-EtOH, 1 mg. R. S. C.

Naphthaquinone oxides. L. F. FIESER, M. TISHLER, and W. L. SAMPSON (J. Amer. Chem. Soc., 1940, 62, 1628—1629).—Oxidation by H₂O₂ yields oily farnesyl- (very weak), phytyl- (active at 500 μ g.) (cleaved by alkali to a mixture of 2-hydroxy-1:4-naphthaquinone and its 3-alkyl derivative), 2:3-dimethyl- (I), m.p. 104—104.5° (active at 25 μ g.), and 3-cinnamyl-2-methyl-, m.p. 85—86°, -1:4-naphthaquinone oxide, and vitamin-K₁ oxide (II), an oil [active at 1.5 μ g.; absorption spectrum resembles that of (I)]. Na₂S₂O₄ in aq. EtOH reduces methyl-naphthaquinone oxide and (II) to 2:1:4-C₁₀H₅Me(OH)₂ and vitamin-K₁ quinol, respectively. The physiological potency of the oxides may be due to their reduction *in vivo*. R. S. C.

Biochemistry of micro-organisms. LXVII. Molecular constitutions of catenarin and erythroglaucon, metabolic products respectively of *Helminthosporium catenarium*, Drechsler, and of species in the *Aspergillus glaucus* series. W. K. ANSLOW and H. RAISTRICK (Biochem. J., 1940, 34, 1124—1133).—Catenarin (I) (A., 1934, 697), which constitutes >15% of the dried mycelium of *H. catenarium*, is reduced by HI (*d* 1.7) and red P in boiling AcOH to emodin anthranol, which is oxidised (aq. AcOH-CrO₃ at 60°) to *Frangula*-emodin [4:5:7-trihydroxy-2-methylanthraquinone]. Methylation (Me₂SO₄, anhyd. K₂CO₃, COMe₂) of (I) gives the Me₄ ether, m.p. 190—191°, oxidised (AcOH-Ac₂O-CrO₃ at 100°) to 3:5:1:2-(OMe)₂C₆H₂(CO)₂O (2%) and 3:6-dimethoxy-4-methylphthalic anhydride (II) (10%), m.p. 202°, thus showing that (I) is 1:4:5:7-tetrahydroxy-2-methylanthraquinone. Erythroglaucon (A., 1939, II, 433) (triacetate, new m.p. 230—231°) is 1:4:5-trihydroxy-7-methoxy-2-methylanthraquinone [catenarin 7-Me ether] and is obtained in good yield from (I) and MeI in MeOH-NaOMe. Toluquinone and aq. KCN in EtOH-conc. H₂SO₄ give 2:5-dihydroxy-3:4-dicyanotoluene, darkens from 195° (black at ~240°) (diacetate, m.p. 128°), methylated (Me₂SO₄, COMe₂, 2N-NaOH) to the Me₂ ether, m.p. 182°, which is hydrolysed by conc. H₂SO₄-H₂O (10:1 vol.) at 100° (bath) to (II). H. B.

Inner complexes. H. M. HAENDLER [with G. MCP. SMITH] (J. Amer. Chem. Soc., 1940, 62, 1669—1672; cf. A., 1939, II, 555).—Absorption max.

of phenanthraquinonemono-oxime, m.p. 161—162°, and its Cd, Cu, Co, Mn, Ni, and UO₂ (also +2EtOH) complexes, chrysenequinonemono-oxime and its Cu, Mn, Ni, UO₂ (also +2EtOH) complexes in C₅H₅N and of benzene-, o-, m-, and p-toluene-, o-, m-, and p-chlorobenzene-, o-, m-, and p-anisole-, o-, m-, and p-phenetole-azo- β -naphthol and their Cu complexes in PhNO₂ are recorded. The substituents have relatively little effect. R. S. C.

Acid-polymerised dipinene. I. Dehydrogenation. J. R. RITTER and J. G. SHAREFKIN. II. Identification of the dehydrogenate. J. R. RITTER and V. BOGERT (J. Amer. Chem. Soc., 1940, 62, 1508—1509, 1509—1511).—I. Dipinene and *dilimonene* (prep. by H₃PO₄ in 71% yield), b.p. 127—128°/1 mm., with S at 200° give a mixture, containing a small amount of 2:6:9-trimethylphenanthrene (I), m.p. 78.2—78.4°, isolated as *picrate*, m.p. 169.5—170°.

II. p-C₆H₄Me·MgBr and menthone in Et₂O give 3-p-tolylmenthol, m.p. 39.5°, b.p. 127—128°/2 mm., $[\alpha]_D^{25}$ -14.49°, dehydrated by H₂C₂O₄ at 150° to 3-p-tolyl- Δ^3 -menthene, b.p. 145—147°/10—11 mm., $[\alpha]_D^{25}$ +49.45°. With S at 220—230° this gives 85% of 3:4-dimethyl-6-isopropylidiphenyl, b.p. 130—132°/4—5 mm. [(NO₂)₃-derivative, m.p. 164—165°], but heating later with S at 320—340° or with Se at 290—360° gives also 2:6:9:9-tetramethylfluorene, b.p. 123—125°/2 mm. [Br-, m.p. 94.5°, and (NO₂)₂-derivative, m.p. 218°], and (I), thereby proving the structure of (I) and accounting for the low yield thereof obtained from the diterpenes. R. S. C.

Saponins and sapogenins. XV. Relationship of echinocystic and oleanolic acids. D. TODD, G. H. HARRIS, and C. R. NOLLER (J. Amer. Chem. Soc., 1940, 62, 1624—1625; cf. A., 1939, II, 333; 1940, II, 18).—Norechino-cystenone or -cystenedione with Zn-Hg-HCl in boiling 95% EtOH gives the oleanene III, obtained (Winterstein *et al.*, A., 1933, 718) from oleanolic acid (I). However, owing to the possibility of rearrangement, echinocystic acid and (I) may have different C-skeletons. R. S. C.

Urechrome, respiratory pigment from eggs of *Urechis caupo*.—See A., 1940, III, 649.

Preparation of 2-furylacetic acid. J. PLUCKER, tert. and E. D. AMSTUTZ (J. Amer. Chem. Soc., 1940, 62, 1512—1513).— α -Thion- β -2-furylpropionic acid [prep. from furfurylidenerhodanin, m.p. 229—231° (decomp.), by alkali], m.p. 114.6—115°, and NH₂OH in boiling abs. EtOH give 81.5—93% of α -oximino- β -2-furylpropionic acid (? *cis*- and *trans*-)forms, m.p. 143.8—144° (decomp.) (lit. 145°) and 121.5—122° (decomp.), which with warm Ac₂O yields 2-furylacetonitrile (82.5—87.7%), b.p. 84°/17 mm., hydrolysed by 18% aq. KOH to 2-furylacetic acid (96%). R. S. C.

Mono- and di-2-furfurylglycine. J. E. ZANETTI and J. T. BASHOUR (J. Amer. Chem. Soc., 1940, 62, 1511—1512).—Furfuryl bromide (1 mol.) and NH₂·CH₂·CO₂Et (2 mols.) in Et₂O (cf. A., 1940, II, 230) give >80% of a mixture, containing 80% of *Et* furfuryl-, b.p. 99—101°/3 mm. [hydrochloride, m.p. 68—70°; *Bz* derivative, b.p. 157—162°/~1 mm.;

hydrolysed by hot H_2O to the derived acid, m.p. 210—212° (corr.), and 20% of *Et di-2-furfuryl-aminoacetate*, b.p. 154—157°/3 mm. [hydrochloride, m.p. 94—96° (corr.); hydrolysed by $\text{Ba}(\text{OH})_2$ or NaOH to the derived acid, m.p. 140—141° (corr.)]. R. S. C.

Synthesis of cestrone. I. 2- β -Phenylethylfurans as components in the diene synthesis. R. B. WOODWARD (J. Amer. Chem. Soc., 1940, **62**, 1478—1482).—2- β -Phenylethylfuran (I), b.p. 241—243°, is best obtained by the method of Freund *et al.* (A., 1890, 1407), but also by (a) condensing 2-furfuryl bromide (II) (purified by MgMeI) with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ and destroying the excess of (II) by MgBuBr before distillation, or (b) condensing furfuraldehyde with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$, dehydrating the crude carbinol by KHSO_4 or $\text{Al}_2(\text{SO}_4)_3$ to ω -2-furylstyrene, m.p. 49—50° (dibromide, m.p. 232.0—232.3°), and finally hydrogenating (PtO_2). $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with $\text{Me}_2\text{SO}_4\text{-NaOH}$ (not CH_3N_2) gives $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, hydrogenated ($\text{PtO}_2\text{-FeSO}_4\cdot\text{EtOH}$; 3 atm.) to $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$, b.p. 150°/25 mm. HBr then gives the bromide, b.p. 116°/8 mm., which with NaCN in aq. EtOH gives *m-anisylacetonitrile* (87.5%), b.p. 164—165°/20 mm. With furfuraldehyde and NaOEt-EtOH this gives α -*m-anisyl- β -2-furylacrylonitrile*, b.p. 180°/1 mm., reduced by Na-EtOH to 2- β -*m-anisylethylfuran* (II), b.p. 153°/10 mm. [also obtained by method (a) as above]. $(\text{CH}\cdot\text{CO})_2\text{O}$ with (I) or (II) gives 3:6-endoxo-3- β -phenyl-, m.p. 73—74° [bromohydroxy-derivative, m.p. 142—143° (decomp.)], and 3:6-endoxo-3- β -*m-anisyl-ethyl- Δ^4 -tetrahydrophthalic anhydride*, m.p. 78—80°. These adducts are unstable, and dissociate when heated or hydrogenated (except with Pt-black in MeOH). R. S. C.

Substituted 2:5-dimesitylfurans. R. E. LUTZ and C. J. KIBLER (J. Amer. Chem. Soc., 1940, **62**, 1520—1528).—2:5-Dimesitylfurans are unique among furan derivatives in resisting oxidative ring-fission to diketones by HNO_3 . Substitution of $\text{C}_{(3)}$ and $\text{C}_{(4)}$ of the furan ring precedes substitution of the mesityl group. Condensation of dimethylfumaryl chloride with 1:3:5:2- $\text{C}_6\text{H}_2\text{Me}_3\text{Br}$ (I) by AlCl_3 in CS_2 is complicated by disproportionation to $s\text{-C}_6\text{H}_3\text{Me}_3$, 1:3:5:2:4- $\text{C}_6\text{HMe}_3\text{Br}_2$, and 1:3:5:2:4:6- $\text{C}_6\text{Me}_3\text{Br}_3$, but when a large excess of (I) is used, 78% of *trans- α -di-3-bromomesityl- β - γ -dimethyl- Δ^8 -butene- α -dione* (II), m.p. 140—143°, is obtained; under other conditions a little *trans- α -mesityl-8:3-bromomesityl- β - γ -dimethyl- Δ^8 -butene- α -dione*, m.p. 124—127°, is isolated. Zn dust in boiling $\text{Ac}_2\text{O-AcOH}$ converts (II) into 2:5-di-4'-bromomesityl-3:4-dimethylfuran (III), m.p. 111.5—113°, best obtained from 2:5-dimesityl-3:4-dimethylfuran (IV) (which with $\text{HNO}_3\text{-AcOH}$ or $\text{-EtCO}_2\text{H}$ at -10° gives a resin) by PBr_5 at 100°. Zn-AcOH does not affect (III), but $\text{H}_2\text{-Pd-BaSO}_4$ gives (IV). (2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHBr}$) $_2$ (prep. from 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ 1:2:4:6 by 8% HBr-AcOH at room temp.) with HBr in CHCl_3 or, less well, AcOH gives 3:4-dibromo-2:5-dimesitylfuran (V), m.p. 139—142°. $(\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3\text{-1:2:4:6})_2$ (VI) and HBr-AcOH at 10° give β -bromo- α -dimesityl-*n-butane- α -dione*, m.p. 81.5—82°, which is reconverted into (VI) by NaOAc or boiling

EtOH . *trans*-(2:4:6:3:1- $\text{C}_6\text{HMe}_3\text{Br}\cdot\text{CO}\cdot\text{CH}$) $_2$ [obtained from (I) and *trans*-($\text{CH}\cdot\text{COCl}$) $_2$ by AlCl_3 ; cf. (II)], m.p. 63—64°, and Br-AcOH at 60—65° give β -*γ-dibromo- α -di-3-bromomesityl-*n-butane- α -dione**, m.p. ~250° (decomp.), which with Zn dust in AcOH gives (2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2$) $_2$ (VII), is unchanged by HBr-AcOH at room temp., but with boiling AcOH or HBr-AcOH gives *trans- β -bromo- α -di-3-bromomesityl- Δ^8 -*n-butene- α -dione**, m.p. 154—155° [reduced by Zn-AcOH to (VII)]. 2:5-Dimesitylfuran (VIII) [prep. from (VII) by HI , but not by other methods] with KMnO_4 gives only a little 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ and by partial bromination gives only a poor yield of (V). 3:4-Dibromo-2:5-di-3'-bromomesitylfuran (IX), forms, m.p. 175—177° and m.p. 166°, resolidifies, remelts at 177°, is obtained from 2:5-di-3'-bromomesitylfuran (X) [prep. from (2:4:6:3:1- $\text{C}_6\text{HMe}_3\text{Br}\cdot\text{CO}\cdot\text{CH}_2$) $_2$ by HI], (VIII), or (V) by PBr_5 at $>90^\circ$ and is reduced by $\text{H}_2\text{-Pd-BaSO}_4$ to (V); at 70° some 3:4-dibromo-2-mesityl-5:3'-bromomesitylfuran, m.p. 125.5—126.5° [with PBr_3 at 90° gives (IX)], is also formed; at 100° PBr_5 converts (VIII) or (IX) into 3:4-dibromo-2:3'-bromomesityl-5:3':5'-dibromomesitylfuran, m.p. 280—282.5°, also obtained from (VIII) by Br-Fe in boiling CS_2 and reduced by $\text{H}_2\text{-Pd-BaSO}_4$ to (V). $\text{HNO}_3\text{-AcOH}$ converts (V) successively into 3:4-dibromo-2-mesityl-5:3'-nitromesityl-, m.p. 121.5—122.5° (Zn dust- AcOH gives a substance, m.p. 150—153°), and -2:5-di-3'-nitromesityl-furan, m.p. 204—205°. Boiling $\text{HNO}_3\text{-AcOH}$ converts (VIII) or 3-nitro-2:5-dimesitylfuran (XI) into 3:4-dinitro-2:5-dimesitylfuran (XII), m.p. 213° [with, from (VIII), a little 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$], which with PBr_5 at 90° gives the 3':3''- Br_2 -derivative (XIII), m.p. 200.5—201.5°. (?) 3-Nitro-2:5-di-3'-bromomesitylfuran (XIV), m.p. 130—130.5°, is obtained from (XI) by PBr_5 at 90—93° or from (V) by boiling 1:3 $\text{HNO}_3\text{-AcOH}$. Boiling 1:1 (vol.) $\text{HNO}_3\text{-AcOH}$ converts (a) (XII) into 3:4-dinitro-2:5-di-3'-nitromesitylfuran (XV), m.p. 266—267°, (b) (X) or (XIV) into a compound, $\text{C}_{22}\text{H}_{17}\text{O}_{11}\text{N}_5\text{Br}_2$, m.p. 287—288°, and (c) (XIII) into 3:4-dinitro-2:5-di-3'-bromo-5'-nitromesitylfuran, m.p. 245° (decomp.; in air), 251—252° (decomp.; vac.) [not obtained by bromination of (XV)]. 1:1 $\text{HNO}_3\text{-AcOH}$ at room temp. converts (VIII) into (?) 3:4-dinitro-2-mesityl-5:3'-nitromesitylfuran, m.p. 158—160°, with a trace of 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$. Finely divided 2:5-diphenyl-3:4-dimethylfuran (XVI) and HNO_3 in EtCO_2H at -10° give *cis- β - γ -dibenzoyl- Δ^8 -butene*, m.p. 86.5—87°, reduced to (XVI) by Zn dust in boiling AcOH . In contrast to the hydrogenations of mesityl compounds, 3:4-dibromo-2:5-di-*p*-bromophenylfuran with $\text{H}_2\text{-Pd-BaSO}_4$ in EtOH yields diphenylfuran. No isomerism due to restricted rotation was noted.

R. S. C.

Syntheses of model unsaturated lactones related to the cardiac aglycones. J. FRIED, M. RUBIN, W. D. PAIST, and R. C. ELDERFIELD (Science, 1940, **91**, 435—436).—Condensation of $\text{Et } \Delta^6\text{-hexenoate}$ with $\text{Et}_2\text{C}_2\text{O}_4$ in presence of KOEt gives $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which, after, hydrolysis, and heating with $\text{HBr} + \text{AcOH}$, yields 5-ethyl- α -pyrone-6-carboxylic acid; this forms (distillation

with Cu) 5-ethyl- α -pyrone. β -Substituted $\Delta^{\alpha\beta}$ -unsaturated γ -lactones containing Ph, cyclohexyl, and Buⁿ groups as representative substituents have been prepared. L. S. T.

Vitamin-E. XXIII. Synthesis of 5-hydroxy-2:4:6:7-tetra- and -2-methyl-coumaran.

Oxidation products of the tetramethylcoumaran.

L. I. SMITH, H. H. HOEHN, and A. G. WHITNEY.

XXIV. Structure of γ -tocopherol. O. H. EMERSON and L. I. SMITH [with, in part, H. E. UNGNADE]

(J. Amer. Chem. Soc., 1940, 62, 1863—1869, 1869—

1872; cf. A., 1940, II, 102).—XXIII. 2:3:5:1-

$C_6H_2Me_3 \cdot OH$ (I), $CH_2 \cdot CH \cdot CH_2Cl$, K_2CO_3 , and, best,

KI give, when boiled, the allyl ether, b.p. 100—103°/

3—4 mm., rearranged, when boiled alone, to

1:2:3:5:6- $OH \cdot C_6HMe_3 \cdot O \cdot CH_2 \cdot CH \cdot CH_2$, m.p. 48—49°,

b.p. 132—133°/12 mm., which with $p\text{-SO}_3H \cdot C_6H_4 \cdot N_2Cl$

gives a dye, whence $Na_2S_2O_4$ at 55° yields 4-amino-

2:3:5-trimethyl-6-allylphenol (II), m.p. 110°. Aq.

$FeCl_3 \cdot HCl$ oxidises (II) to 2:3:5-trimethyl-6-allyl-

1:4-benzoquinone, b.p. 108°/1 mm., whence Zn-AcOH

gives the quinol, m.p. 137—138°, which with

$C_5H_5N \cdot HCl$ at 135° yields 5-hydroxy-2:4:6:7-

tetramethylcoumaran (III). AgOAc in boiling MeOH

converts (III) into 2:3:5-trimethyl-6- β -hydroxy-

propyl- p -benzoquinone, m.p. < room temp., which

with Zn dust- $NaOAc \cdot Ac_2O$ gives 2:3:5-trimethyl-6-

β -acetoxypropylquinol diacetate (IV), m.p. 92—93°.

AgNO₃ in EtOH oxidises (III) to 2:4:6-trimethyl-

coumaran-4:5-quinone, red, m.p. 83—87°, 96—97°,

or 104—105°, unstable. Interaction with p -

$SO_3H \cdot C_6H_4 \cdot N_2Cl$ and then $Na_2S_2O_4$ converts (I) into

4-amino-2:3:5-trimethylphenol (V), m.p. 152—153°,

the Ac derivative, m.p. 184—185°, of which with

$NaOEt \cdot CH_2 \cdot CH \cdot CH_2Cl \cdot EtOH$ gives 4-acetamido-

2:3:5-trimethylphenyl allyl ether, m.p. 165—165.5°,

rearranged in kerosene at 225° to 4-acetamido-2:3:5-

trimethyl-6-allylphenol, m.p. 206—207° (gives no

quinone with $FeCl_3$), which in boiling 40% HBr gives

5-acetamido-2:4:6:7-tetramethylcoumaran (VI), m.p.

203° (stable also to $MgMeBr$). The N-CHO deriv-

ative, m.p. 213°, of (V) gives similarly the allyl ether,

m.p. 162—162.5°, and 4-formamido-2:3:5-trimethyl-

6-allylphenol, m.p. 183—184°, which in boiling 40%

HBr gives 5-amino-2:4:6:7-tetramethylcoumaran,

m.p. 77—78° [Ac derivative = (VI)]. The hydro-

bromide, m.p. >320°, thereof is oxidised by $FeCl_3 \cdot$

$HCl \cdot H_2O$ to 2:3:5-trimethyl-6- β -hydroxypropyl-

1:4-benzoquinone, m.p. 54—55° (lit. 56.5°), and

thence yields (Zn-AcOH) 2:3:5-trimethyl-6- β -hydr-

oxypropylquinol, m.p. 137—138° [triacetate = (IV)],

and (HBr-AcOH and a little Zn dust) (III).

$CH_2 \cdot CH \cdot CH_2 \cdot OPh$ is obtained in 74% yield from

$PhOH$ by $CH_2 \cdot CH \cdot CH_2Cl$ and K_2CO_3 in $COMe_2$ and,

when boiled, gives 76% of $o\text{-OH} \cdot C_6H_4 \cdot CH_2 \cdot CH \cdot CH_2$,

which by $p\text{-SO}_3H \cdot C_6H_4 \cdot N_2Cl$ and then $Na_2S_2O_4$ gives

2:1:4- $CH_2 \cdot CH \cdot CH_2 \cdot O \cdot C_6H_3(OH) \cdot NH_2$, m.p. 113—

114°. Careful oxidation then gives allyl- p -benzo-

quinone, b.p. 102—103°/18 mm. [only a trace is

obtained from 2:1:4- $CH_2 \cdot CH \cdot CH_2 \cdot O \cdot C_6H_3(OH) \cdot NO$,

m.p. 93—94° (lit. 100—101°), by $H_2O_2 \cdot HCl \cdot H_2O$],

and the mother-liquors, when reduced by $Na_2S_2O_4$,

give allylquinol (VII), m.p. 91—92°, b.p. 161°/10 mm.

(diacetate, m.p. 47—48°). Cyclisation of (VII) by

H_2O (not $C_5H_5N \cdot HCl$) gives 5-hydroxy-2-methyl-

coumaran, m.p. 66—67°, b.p. 150—154°/14—15 mm.

(oily benzoate and acetate).

XXIV. γ -Tocopherol (I) (p -nitrophenylurethane,

m.p. 119—121°; benzylthiuronium succinate, m.p.

104—105°) is shown to be 7:8-dimethyltolcol [α -

xytolocopherol]. Oxidation gives $(CMe \cdot CO)_2O$. It

is synthesised from 1:2:3:4- $OH \cdot C_6H_2Me_2 \cdot OBz$,

phytyl bromide, and $ZnCl_2$ in boiling C_6H_6 . 5:8-

Dimethyltolcol (p -nitrophenylurethane, m.p. 111—

112°; benzylthiuronium succinate, m.p. 104—106°)

is similarly obtained; its derivatives do not depress

the m.p. of those of (I). Allylation of (I) gives an

oily, mainly tricyclic substance, $C_{31}H_{52}O_2$. R. S. C.

Interaction of o -hydroxybenzhydrylaceto-

phenone and o -hydroxybenzylidenediacetophenone

with magnesium phenyl bromide. T. A. GEISS-

MAN (J. Amer. Chem. Soc., 1940, 62, 1363—1367).—

Contrary to statements of Löwenbein (A., 1924, i,

1221), $o\text{-OH} \cdot C_6H_4 \cdot CHPh \cdot CH_2 \cdot C(=O)Ph$, new m.p. 167—

167.5° (derived pyrylium ferrichloride, new m.p.

167°), gives a semicarbazone, m.p. 177—178°, and

dissolves in $KOH \cdot MeOH$. It also reacts as the

phenol with $MgPhBr$ in boiling Et_2O , yielding $\alpha\alpha$ -

triphenyl- γ - o -hydroxyphenyl- n -propyl alcohol (I), m.p.

(anhyd.) 112—113°, (+ ? C_6H_6) $\sim 85^\circ$, obtained also

from 4-phenyldihydrocoumarin by $MgPhBr$ in C_6H_6 -

Et_2O and dehydrated by hot $H_2SO_4 \cdot AcOH$ to 2:2:4-

triphenylchroman (II), m.p. 162—163°. o -

$OH \cdot C_6H_4 \cdot CH(CH_2 \cdot C(=O)Ph)_2$ (III) and $MgPhBr$ in

Et_2O at 5—10° give an oil, probably o -

$OH \cdot C_6H_4 \cdot CH(CH_2 \cdot C(=O)Ph) \cdot CH_2 \cdot CPh_2 \cdot OH$, which in

(best) $AcOH$ gives the compound (IV), m.p. 185—

186°, believed by Gomm *et al.*

(A., 1935, 1377) to be (I). In

boiling C_6H_6 , (III) and $MgPhBr$

give an oil, o -

$OH \cdot C_6H_4 \cdot CH(CH_2 \cdot CPh_2 \cdot OH)_2$,

converted by $H_2SO_4 \cdot AcOH$ into

2:2-diphenyl-4-benzhydrylidene-

methylchroman (V), m.p. 219—220°, which is also

obtained from the mother-liquors of (IV) by $H_2SO_4 \cdot$

$AcOH$ and was considered (*loc. cit.*) to be (II). A little

H_2SO_4 in boiling $AcOH$ isomerises 2-phenyl-4- β -

hydroxy- $\beta\beta$ -diphenylethylflavene (VI), m.p. 193—

193.5° (*loc. cit.* 194°), or (IV) to 2:2-diphenyl-4-

phenacylchroman, m.p. 115—116° [2:4-dinitrophenyl-

hydrazone, m.p. 243—244° (decomp.), obtained also

directly from (IV) or (VI)], which with $MgPhBr$ in

boiling Et_2O gives 2:2-diphenyl-4- β -hydroxy- $\beta\beta$ -

phenylethylchroman, m.p. 149—149.5°, converted by

$H_2SO_4 \cdot AcOH$ into (V). The structure of (V) is

proved by synthesis from *Me dihydrocoumarin-4-*

acetate, b.p. 208—210°/20 mm., by $MgPhBr$ in Et_2O .

R. S. C.

Osage orange pigments. IV. Degree of un-

saturation and flavone nature. M. L. WOLFROM,

P. W. MORGAN, and F. L. BENTON (J. Amer. Chem.

Soc., 1940, 62, 1484—1489; cf. A., 1940, II, 185).—

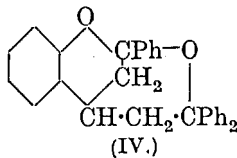
Hydrogenation (PtO_2) converts osajin successively

and with increasing difficulty into a H_2 -, m.p. 197°

(mono-, m.p. 156.5°, and di-acetate, m.p. 154°), H_4 -,

m.p. 198—200° (mono-, m.p. 179.5°, and di-acetate,

m.p. 186°), and H_6 -derivative, m.p. 162° (mono-, m.p.



138°, and *di-acetate*, m.p. 190°). Pomiferin similarly gives H_2 , m.p. 212° (*di*-, m.p. 166°, and *tri-acetate*, m.p. 165.5°), and H_4 -derivatives, m.p. 201.5° (*di*-, m.p. 154.5°, and *tri-acetate*, m.p. 181.5°). These reactions, BzO_2H titrations, H_3BO_3 colours, Na-Hg and Mg-Hg reductions, and failure of diene additions indicate 5-hydroxyflavone structures. R. S. C.

2:2'-Pyridyl disulphide and 2-thiolhexamethyleneimine.—See B., 1940, 552.

Direct synthesis of 2-hydroxy-3-cyanopyridine and its 6-methyl derivative. A. DORNOW (Ber., 1940, 73, [B], 153—156).— $OEt\cdot CH\cdot CH\cdot CH(OEt)_2$ with $CN\cdot CH_2\cdot CO\cdot NH_2$ and piperidine in 95% EtOH at the b.p. gives the piperidine additive compound, m.p. 197°, of *2-hydroxy-3-cyanopyridine* (I), m.p. 225—226° (isolated after treatment with boiling N-NaOH). With conc. HCl at the b.p., (I) gives 2-hydroxynicotinic acid (*Et* ester, m.p. 139°; *anilide*, m.p. 261°; *amide*, m.p. 266—267°). Similarly $OEt\cdot CMe\cdot CH\cdot CH(OEt)_2$ gives the piperidine salt, m.p. 192°, of *2-hydroxy-3-cyano-6-methylpyridine*, m.p. ~295° (decomp.), hydrolysed to *2-hydroxy-6-methyl-nicotinic acid*, m.p. 228°, which above its m.p. gives 2-hydroxy-6-methylpyridine. E. W. W.

Organic peroxides. VII. Dinicotinoyl peroxide. N. A. MILAS and P. C. PANAGIOTAKOS (J. Amer. Chem. Soc., 1940, 62, 1878; cf. A., 1939, II, 503).—Nicotinoyl chloride, Na_2O_2 , ice, and Et_2O (not $H_2O_2\cdot Et_2O$) at 0° to -5° give *dinicotinoyl peroxide*, m.p. 88—89°, resolidifies, remelts at 175°.

R. S. C.

Derivatives of 4-pyridylphthalic acids.—See B., 1940, 594.

Oxidation of β -phenylethylpyridinium salts. II. S. SUGASAWA and N. LEE (Proc. Imp. Acad. Tokyo, 1940, 16, 187—190; cf. A., 1939, II, 281).—Oxidation [alkaline $K_2Fe(CN)_6$] of β -*o*-methoxyphenylethylpyridinium bromide (corresponding *picrate*, m.p. 114—115°) smoothly yields 1- β -*o*-methoxyphenylethyl-2-pyridone, m.p. 130—131°, and β -2:3-dimethoxyphenylethylpyridinium bromide (corresponding *picrate* m.p. 111—112°) gives 1- β -2':3'-dimethoxyphenylethyl-2-pyridone. The latter compound is converted into 3':4'-dimethoxy-3:4-dihydro-9:10-dehydro-(1':2':1:2-benzopyridocolinium) salt on ring-closure, characterised as the *iodide*, m.p. 182°. The corresponding H_4 -derivative is characterised as the hydriodide and *picrate*. β -3:4-Dimethoxy-6-methylphenylethylpyridinium bromide, m.p. 154—156°, is smoothly oxidised to 1- β -3':4'-dimethoxy-6'-methylphenylethyl-2-pyridone, which is readily transformed by $POCl_3$ into HCl and 5':6'-dimethoxy-3'-methyl-3:4-dihydro-9:10-dehydro-(1':2':1:2-benzopyridocolinium) *iodide*, m.p. 186—187°. β -2:5-Dimethoxyphenylethylpyridinium bromide, m.p. 53—54°, is oxidised to 1- β -2':5'-dimethoxyphenylethyl-2-pyridone, which gives 3':6'-dimethoxy-3:4-dihydro-9:10-dehydro-(1':2':1:2-benzopyridocolinium) *iodide*, m.p. 156—157°.

H. W.

Formation of Reissert's compounds in non-aqueous media. R. B. WOODWARD (J. Amer. Chem. Soc., 1940, 62, 1626—1627).— $BzCl$ or $CHPh\cdot CH\cdot COCl$ with quinoline (I) and KCN in liquid

SO_2 gives 1-benzoyl-, m.p. 154—155°, and 1-cinnamoyl-1:2-dihydroquinaldine-2-nitrile, m.p. 149—150°, but $AcCl$ gives a mixture. $BzCl$ with HCN and (I) gives mainly $BzCN$. $AcCl$ gives only $AcCN$ in Et_2O , other inert solvents, or excess of (I). No reaction occurs with KCN and (I) in MeCN, PhCN, Et_2O , dioxan, $COMe_2$, or $CHCl_3$. The reaction is probably ionic. R. S. C.

Phenanthridine derivatives.—See B., 1940, 516.

Metallic complex salts of 2:2'-dipyridyl.—See A., 1940, I, 344.

Differences observed in the behaviour of unsaturated hydantoin towards bromine. (MISSES) M. J. McLEAN and D. R. SEEGER (J. Amer. Chem. Soc., 1940, 62, 1416—1419).—5-Benzylidene-3-methylhydantoin (I) and Br in CCl_4 give 5-bromo-5- α -bromobenzyl-3-methylhydantoin (II), m.p. 153—154° (later decomp.), which at room temp. slowly or at 105° rapidly loses HBr to give 5-bromo-5-benzylidene-3-methylhydantoin (III), m.p. 173—173.5°, and in warm EtOH gives HBr and 5-ethoxy-5- α -bromobenzyl-3-methylhydantoin (IV), m.p. 179—180°. (III) is obtained from (I) by Br in AcOH, and (IV) is obtained without isolating (II) by adding EtOH to the CCl_4 reaction mixture. 5-Benzylidenehydantoin in CCl_4 gives a sol. dibromide, m.p. 178—182° (gas), solidifies, remelts at ~235° (5-bromo-5-benzylidenehydantoin melts at 239—240°), which with EtOH gives HBr and 5-ethoxy-5- α -bromobenzylhydantoin, m.p. 202.5—203°. 5-Benzylidene-1:3-dimethylhydantoin and Br in AcOH give 5- α -bromobenzyl-1:3-dimethylhydantoin, m.p. 122—123°. These reactions clarify reports in the literature. The 5- α -bromobenzylalkylhydantoin are reduced by HI-red P to the corresponding benzylalkylhydantoin. R. S. C.

Synthesis of intermediate metabolic products of histidine. I. Synthesis of urocanic acid. S. AKABORI, S. OSE, and T. KANEKO (Proc. Imp. Acad. Tokyo, 1940, 16, 191—194).—Aeration of a solution containing invert sugar, $CuSO_4$, NaOH, and NH_3 gives 4(5)-hydroxymethylglyoxaline, m.p. 92° (*picrate*, m.p. 205°), oxidised by conc. HNO_3 at 100° to glyoxaline-4(5)-carboxylic acid and *aldehyde* (I), m.p. 173°. $CH_2(CO_2H)_2$ and (I) in H_2O at ~50° yield 4(5)- β -dicarboxyvinylglyoxaline, m.p. 212° (decomp.), which passes in boiling C_5H_5N into urocanic acid, m.p. 230—231° (decomp.), reduced to glyoxaline-4(5)-propionic acid (hydrochloride, m.p. 83°).

H. W.

New heterovitamin-B₁, 1-(4'-amino-2'-methyl-5'-pyrimidylmethyl)-3- β -hydroxyethylpyridinium bromide. A. DORNOW (Ber., 1940, 73, [B], 156—158; cf. A., 1940, II, 291).—Nicotinoyl chloride hydrochloride in Et_2O with 3 CH_2N_2 at 0—5° gives 3-diazoacetylpyridine, m.p. 74° [*picrate*, m.p. 155—156° (decomp.)], which when heated with AcOH gives 3-acetoxyacetylpyridine, m.p. 84—85° (*picrate*, m.p. 158°), which is reduced (Zn-HCl) to 3- β -hydroxyethylpyridine, b.p. 133°/12 mm. (*urethane*, m.p. 147°). This with 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide in $MeNO_2$ at ~40° gives 1-(4'-amino-2'-methyl-5'-pyrimidylmethyl)-3- β -hydroxyethylpyridinium bromide hydrobromide, m.p. 244—245°

(decomp.). This compound has only 1/240 of the vitamin activity of aneurin. E. W. W.

2 : 3-Bis-(2'-benziminazolyl)pyridine. A. M. LECCO and D. M. DIMITRIJEVIĆ (Ber., 1940, 73, [B], 108—111).—The by-product from quinolinic acid and α -C₆H₄(NH₂)₂ (I), regarded by Bistrzycki and Lecco (A., 1921, i, 456) as 2-(3'-pyridyl)benziminazole, is 2 : 3-bis-(2'-benziminazolyl)pyridine, m.p. 313° (Ag₂ salt), also obtained from 2-(2'-benziminazolyl)pyridine-3-carboxylic acid and (I), or from nicotinoylenebenziminazole and (I), and treatment of the resulting 2-(2'-benziminazolyl)pyridine-3-carboxyl- α -aminoanilide, m.p. 249—250°, with AcOH. E. W. W.

Raman effect and constitution of methylated benztriazole and indazole.—See A., 1940, I, 346.

Phthalocyaninesulphonamides.—See B., 1940, 517.

Method of separating small quantities of coproporphyrin isomerides I and III. C. J. WATSON and S. SCHWARTZ (Proc. Soc. Exp. Biol. Med., 1940, 44, 7—10).—The Me esters are adsorbed on to Brockmann's Al₂O₃. Isomeride III ester is then dissolved in 35% aq. COMe₂; isomeride I ester is dissolved later in pure COMe₂. V. J. W.

Ethers and amines from β -4-morpholinoethyl chloride. J. P. MASON and S. MALKIEL (J. Amer. Chem. Soc., 1940, 62, 1448—1450).—4- β -Chloroethylmorpholine hydrochloride and NaOR in boiling ROH give 4- β -methoxy-, b.p. 104—105.8°/44 mm. (also obtained by KOH-MeOH), -ethoxy-, b.p. 96—99°/17—19 mm., -n-, b.p. 120—123°/23 mm., and -isopropoxy-, b.p. 115—120°/34—35 mm., -n-, b.p. 134.5—137.5°/31 mm., -sec-, b.p. 105.5—108.5°/7—8 mm., and -tert.-butoxy-, b.p. 113—116°/19 mm., -benzyloxy-, b.p. 196—202°/30—32 mm., and -phenoxy-ethylmorpholine (by PhOH in aq. NaOH), b.p. 181—183°/21—22 mm., and di-(β -morpholinoethyl) ether (prep. at 200°), b.p. 178—180.5°/7 mm. (picrate, m.p. 175°). 4- β -Chloroethylmorpholine (I) with aq. NH₃ or NH₂Bu^a at 93—98° gives 4- β -amino-, b.p. 82°/6 mm. [picrate, m.p. 188° (corr.)], and 4- β -n-butylamino-ethylmorpholine, b.p. 136—140°/20—21 mm. [picrate, m.p. 180.5° (corr.)]. (I) and the appropriate base at 200° give 4- β -anilinoethylmorpholine, b.p. 186—188.5°/9 mm. [picrate, m.p. 138—140.6° (corr.)], and $\alpha\beta$ -dimorpholinoethane, m.p. 73° (lit. 74°) [picrate, m.p. 234—237° (lit. 230—236°)]. R. S. C.

4-Morpholinoethyl alkyl ethers and N-substituted morpholines. J. P. MASON and M. ZIEF (J. Amer. Chem. Soc., 1940, 62, 1450—1452).—Morpholine (I) (1 mol.), paraformaldehyde (1 mol.), and ROH (2 mols.) in C₆H₆ at (usually) 100° give 4-methoxy- (46.2%), b.p. 55.6—57°/8 mm., -ethoxy- (II) (59.3%), b.p. 58—63°/6 mm., -n- (74%), b.p. 100—102°/22 mm., and -iso-propoxy- (29.7%), b.p. 64—66°/6 mm., -n- (73.8%), b.p. 99.5—100.5°/11 mm., -iso- (68%), b.p. 90.5—92.5°/10 mm., -sec- (58.9%), b.p. 92—94°/10 mm., and -tert.-butoxy- (9.4%), -allyloxy- (52.4%), b.p. 82—83°/7 mm., and -benzyloxy- (76.8%), b.p. 152—154°/7 mm., -methylmorpholine; the remainder of the (I) appears as di-4-morpholinomethane. MgRHal in Et₂O converts (II) into 4- β -phenylethyl- (66%), b.p. 147—151°/13 mm. (picrate,

m.p. 166—167°), - α -naphthylmethyl- (57.7%), b.p. 185—190°/9 mm. (picrate, m.p. 209—211°), -n-propyl- (43.4%), b.p. 43—46°/7 mm. (picrate, m.p. 118—120°), -n-hexyl- (59.7%), b.p. 86—87°/6 mm. (picrate, m.p. 110—111°), and -benzyl- (64.4%), b.p. 135—136.5°/14 mm. (picrate, m.p. 193.5—196°), -morpholine. M.p. are corr. R. S. C.

Preparation and polymerisation of β -4-morpholinoethyl chloride. J. P. MASON and H. W. BLOCK (J. Amer. Chem. Soc., 1940, 62, 1443—1448).—4- β -Chloroethylmorpholine (I), b.p. 93—94°/12 mm. (hydrochloride, m.p. 182—182.5°; picrate, m.p. 130°), is obtained by SOCl₂ from 4- β -hydroxyethylmorpholine (73—88%) (picrate, m.p. 126°) or the hydrochloride (63.5%), m.p. 109—110° (softens at 100°). When kept or heated, (I) gives slowly 1 : 4-dispiromorpholinopiperazinium dichloride (II), a solid, which is obtained rapidly in hot ROH with large amounts of 4- β -ethoxy- (hydrochloride, m.p. 138°; picrate, m.p. 103°) and 4- β -n-propoxy-ethylmorpholine (hydrochloride, m.p. 130—131°). (I) does not polymerise in dioxan, but addition of increasing amounts of H₂O increases the amount of (II) formed, which is connected with the increase in dielectric const., although none is formed in Et₂O or C₆H₆ and very little in COMe₂. Mg does not react with (I) but catalyses the polymerisation. The structure of (I) is proved by fission by 50% aq. KOH to C₂H₂ and $\alpha\beta$ -dimorpholinoethane, m.p. 73.5° (lit. 74°) [picrate, new m.p. 234—236° (decomp.)]. R. S. C.

Thiamorpholine [thiazane, tetrahydro-1 : 4-thiazine] series. II. N-Alkyl derivatives. (MISS) H. I. MINER, E. O. HOOK, and R. D. COGHILL. III. Derivatives of tetrahydro-1 : 4-thiazine-3 : 5-dicarboxylic acid. E. O. HOOK, (MISS) H. I. MINER, and R. D. COGHILL (J. Amer. Chem. Soc., 1940, 62, 1613—1614, 1615—1616; cf. A., 1937, II, 309).—II. Passage of NH₃ or NH₂R into S(CH₂CHO)₂, HCN, and a little piperidine and consequent rise of temp. to 70° gives tetrahydro-1 : 4-thiazine-3 : 5-dinitrile, m.p. 214° (decomp.), 4-methyl-, m.p. 178°, 4-ethyl-, m.p. 137°, and 4-benzyl-tetrahydro-1 : 4-thiazine-3 : 5-dinitrile, m.p. 170°. If the temp. is maintained at <10°, 4-methyl- (I), m.p. 208° (decomp.), 4-ethyl-, m.p. 177° (decomp.), 4-n-butyl-, m.p. 192° (decomp.), 4-n-amyl-, m.p. 174° (decomp.), 4-iso-amyl-, m.p. 192° (decomp.), and 4-n-heptyl-, m.p. 181° (decomp.), tetrahydro-1 : 4-thiazine-3-nitrile-5-carboxylamide are obtained. Conc. HCl at 10° converts (I) into 4-methyltetrahydro-1 : 4-thiazine-3-nitrile-5-carboxylic acid, m.p. 184—185°, but other hydrolyses fail.

III. Tetrahydro-1 : 4-thiazine-3 : 5-dicarboxylic acid (loc. cit.) with 30% H₂O₂ in AcOH-Ac₂O at 0° gives the 1-oxide, m.p. 242° (decomp.), with boiling Ac₂O gives the 4-Ac derivative, m.p. 143° (decomp.), gives a carbobenzyloxy-derivative, m.p. 149.5—150°, and Et₂ ester, b.p. 154—156°/3 mm., and thence the di- β -diethylaminoethyl [trihydrochloride, m.p. 208° (decomp.)] and di- γ -diethylaminopropyl [trihydrochloride, m.p. 215° (decomp.)] esters, and (by NEt₂[CH₂]₂NH₂ at 160—170°) tetrahydro-1 : 4-thiazine-3 : 5-di(carboxyl- β -diethylaminoethylamide), decomp. ~245°. M.p. (both parts) are corr.

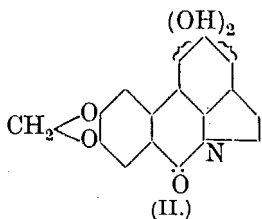
R. S. C.

Rubber vulcanisation accelerators. VI. Mechanism of and methods for the synthesis of thiolbenzthiazole from methylenedianiline. Y. KAWAOKA (J. Soc. Chem. Ind. Japan, 1940, 43, 151—153B).— $\text{NPh}\cdot\text{CH}_2$ with S under pressure at 130° yields H_2S , CS_2 , a trace of NH_2Ph , but no PhNCS or $\text{NPh}\cdot\text{CH}\cdot\text{NHPh}$ (I); at 200 — 250° , the main product is PhNCS . $\text{NPh}\cdot\text{CH}_2$ with S in CS_2 , with or without NH_2Ph , at 220 — 240° under pressure yields 75% of thiolbenzthiazole (II), obtained in 77% yield from (I), S, and CS_2 at 249° under pressure. PhNCS with S at 260° under pressure yields only 0.12%, or with CS_2 1.0%, of (II). PhNC with S and CS_2 under pressure yields no (II) at 151° , and very little at 180° . The mechanism of the formation of (II) is discussed.

A. LI.

Photographic sensitisers.—See B., 1940, 568.

Lycoris alkaloids. XV. Constitution of lycorine. VII. H. KONDO and H. KATSURA (Ber., 1940, 73, [B], 112—115; cf. A., 1940, II, 144).—Dihydrolycorine (I) with 3% KMnO_4 at 1 — 2° gives dihydrolycorinone (II) (annexed formula), m.p. 246° , better obtained by oxidising (KMnO_4 in COMe_3) the Ac_2 derivative of (I) to the Ac_2 derivative (III), m.p. 130° , of (II), to which (III) is hydrolysed. (II) is not affected by SeO_2 in AcOH , or by $\text{K}_2\text{OsO}_4(\text{OMe})_4$. With $\text{K}_2\text{Cr}_2\text{O}_7$ — H_2SO_4 , (II) in AcOH gives a compound, decomp. 186° . With $\text{Pb}(\text{OAc})_4$ in C_6H_6 at the b.p., (II) gives, after treatment with NH_2OH , a dialdehyde dioxime, decomp. 233° , or, after treatment with Ac_2O at 50° , an aldehydo-acid, $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}(\text{CHO})\cdot\text{CO}_2\text{H}$, decomp. 245° , and a neutral product. E. W. W.



Strychnine alkaloids. CIX. Reaction of the nitroquinone from N-methyl-ψ-brucine; other nitroquinones of this series. H. LEUCNS and H. G. BOHR (Ber., 1940, 73, [B], 99—103; cf. A., 1939, II, 232, 489).—N-Methyl-sec-ψ-brucine (I) in 10N-HNO_3 (containing HNO_2) at -10° with aq. picric acid gives the picrate, $\text{C}_{22}\text{H}_{22}\text{O}_5\text{N}_2\cdot\text{HNO}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, of the o-quinone (II) [perchlorate (extracted by CHCl_3 after addition of KHCO_3)] of (I). With $\text{NH}_2\text{OH}\cdot\text{HCl}$, (II) gives its oxime hydrate hydrochloride (III), $\text{C}_{22}\text{H}_{25}\text{O}_6\text{N}_3\cdot 2\text{HCl}$, reduced by Zn — HCl to the stannichloride, sinters 270 — 280° (to a black resin), of aminohydroxy-N-methyl-sec-ψ-strychnine. With HClO_4 and Zn , followed by H_2O_2 , (III) gives an amorphous oxazine colouring matter. The HNO_3 solution of (I), with HClO_4 and SO_2 at -10° , gives the o-quinol hydrate perchlorate, $\text{C}_{22}\text{H}_{26}\text{O}_6\text{N}_2\cdot\text{HClO}_4$, of (I). The same solution with HClO_4 , heated to 50° , gives a nitroquinone hydrate perchlorate, $\text{C}_{22}\text{H}_{23}\text{O}_8\text{N}_3\cdot\text{HClO}_4$ (+0.5 or $1\text{H}_2\text{O}$) (IV), reduced by Sn — HCl to the aminoquinol stannichloride, $\text{C}_{22}\text{H}_{25}\text{O}_6\text{N}_3\cdot 2\text{HCl}\cdot\text{SnCl}_4$, or by SO_2 to the nitroquinol perchlorate, $\text{C}_{22}\text{H}_{25}\text{O}_8\text{N}_3\cdot\text{HClO}_4\cdot 0.5\text{H}_2\text{O}$ [oxidised by HNO_3 to (IV)]. With $\text{NH}_2\text{OH}\cdot\text{HCl}$, (IV) gives the oxime hydrochloride, $\text{C}_{22}\text{H}_{24}\text{O}_8\text{N}_4\cdot\text{HCl}$. In H_2O at 80° , (IV) gives a red dimeride, m.p. $\sim 145^\circ$ (to a resin); when the solution is heated with HClO_4 a yellowish-red salt, $\text{C}_{22}\text{H}_{23}\text{O}_8\text{N}_3\cdot\text{HClO}_4\cdot\text{H}_2\text{O}$, m.p. 145° (decomp.),

is obtained. N-Methyl-sec-ψ-brucine methoperechlorate with 8N-HNO_3 at 60° , followed by HClO_4 , gives the methoperechlorate, $\text{C}_{22}\text{H}_{23}\text{O}_8\text{N}_3\cdot\text{MeClO}_4\cdot 0.5\text{H}_2\text{O}$ (V), analogous to (IV). The ether, $\text{C}_{25}\text{H}_{22}\text{O}_5\text{N}_2$, similarly gives a nitroquinol hydrate, $\text{C}_{23}\text{H}_{22}\text{O}_8\text{N}_3\cdot\text{HClO}_4\cdot 0.5\text{H}_2\text{O}$ (VI). Neither (V) nor (VI) gives any coloured dimeride or isomeride when heated with H_2O ; the formation of such a compound from nitroquinol hydrates of the ψ-brucine series appears to require the presence of the $\cdot\text{C}(\text{OH})\cdot\text{N}\cdot$ system. E. W. W.

Veratrine alkaloids. VII. Decevinic acid.

L. C. CRAIG and W. A. JACOBS (J. Biol. Chem., 1940, 134, 123—135).—Decevinic acid (I), $\text{C}_{14}\text{H}_{14}\text{O}_6$ (A., 1939, II, 490) (prep. from cevine described), with S at 300° yields 2-hydroxy-1:8-naphthoic anhydride, which with conc. NaOH gives $2:8\text{-OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ (identified as Me ether). (I) neutralises only 2 NaOH in the cold, the product on acidification giving an acid, $\text{C}_{13}\text{H}_{16}\text{O}_5$, m.p. 150 — 155° (efferv.) [Me_2 ester (CH_2N_2)], which gives no reaction with FeCl_3 , is neutralised by 2 NaOH , and when distilled, or heated with N-NaOH and acidified, yields a ketolactone (II), $\text{C}_{12}\text{H}_{16}\text{O}_3$, m.p. 165 — 168° , $[\alpha]_{\text{D}}^{25} -50^\circ$ in CHCl_3 (phenylhydrazone, m.p. 175 — 178° ; oxime, m.p. 194 — 195° after sintering), which reacts with 1 NaOH , but not with Na_2CO_3 or CH_2N_2 . The Me ester (III), $\text{C}_{16}\text{H}_{18}\text{O}_6$, of (I) when boiled with N-NaOH and acidified yields (II). The Ac derivative, m.p. 169 — 171° , of (I) with CH_2N_2 yields the Ac derivative, m.p. 182 — 183° , of decevinic acid Me_1 ester, $\text{C}_{15}\text{H}_{16}\text{O}_6$, m.p. 242 — 245° . Partial hydrolysis (warm NaOH) of (III) yields a substance, $\text{C}_{15}\text{H}_{16}\text{O}_6$, m.p. 128° , which gives no Ac derivative. (I) with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ yields a compound, $\text{C}_{20}\text{H}_{20}\text{O}_5\text{N}_2$, m.p. 300 — 302° , which is neutralised by 1 NaOH , and gives no reaction with FeCl_3 . Hydrogenation (PtO_2) of (I) followed by distillation (with loss of H_2O) at 0.1 mm. yields a monobasic lactone acid, $\text{C}_{14}\text{H}_{20}\text{O}_4$, m.p. 237 — 239° [Me ester (CH_2N_2), m.p. 127 — 128°]. Hydrogenation and distillation of (II) yields two substances, $\text{C}_{12}\text{H}_{18}\text{O}_2$ (?), m.p. 97° , and $\text{C}_{12}\text{H}_{18}\text{O}_3$ (?), m.p. 65 — 73° (a few crystals persisting to 90°). The constitution of (I) is discussed. A. LI.

Structure of acetocodeine. L. SMALL and J. E. MALLONEE (J. Org. Chem., 1940, 5, 286—289).—Attempts to rearrange aceto-6-acetylcodeineoxime with conc. H_2SO_4 or PCl_5 under the usual conditions give unchanged material or cause extensive decomp. With Beckmann's mixture at room temp. rearrangement gives acetamido-6-acetylcodeine [trihydrate, m.p. 112 — 115° (decomp.), $[\alpha]_{\text{D}}^{20} -214^\circ$ in EtOH], hydrolysed to 1-aminocodeine, m.p. 223 — 226° , $[\alpha]_{\text{D}}^{25} -181.1^\circ$ in H_2O . Acetocodeine therefore has Ac at C_{11} . H. W.

Relative reactivities of organo-metallic compounds. XXXI. Alkali benzyl compounds. H. GILMAN, H. A. PACEVITZ, and O. BATNE (J. Amer. Chem. Soc., 1940, 62, 1514—1520; cf. A., 1940, II, 172, 276).—The formation of organo-alkali compounds named below is proved by interaction with CO_2 to give the derived acid. *o*-, *m*-, or *p*- $\text{Hg}(\text{C}_6\text{H}_4\text{Me})_2$ and Na in boiling light petroleum or PhMe give NaCH_2Ph , but reaction is very slow at room temp.; the reaction mechanism for the *m*-compound is obscure. PhCl

and Na in PhMe at $\pm 40^\circ$ give NaPh. HgPh_2 and Na in C_6H_6 in 24 hr. at room temp. give, after interaction with CO_2 , 86% of BzOH , but 62% if boiled for 24 hr. Na and $p\text{-C}_6\text{H}_4\text{MeCl}$ in various solvents at $35\text{--}40^\circ$ give 56–80% of $p\text{-C}_6\text{H}_4\text{MeNa}$, but when boiled give 48.5–79% of NaCH_2Ph . KCH_2Ph is prepared from, best, (a) K sand and PhCl in PhMe at $30\text{--}35^\circ$, (b) HgBu^a_2 and K in C_6H_6 and then PhMe, or, least well, (c) $\text{Hg}(\text{C}_6\text{H}_4\text{Me-}p)_2$ and K in boiling light petroleum; passing CO_2 over the surface of the solution prepared as in (a) gives 55% of $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ and 23% of $\text{CHPh}(\text{CO}_2\text{H})_2$. KCH_2Ph and COPh_2 give $\text{CH}_2\text{Ph}\cdot\text{CPh}_2\cdot\text{OH}$. PhCl and K in $s\text{-C}_6\text{H}_3\text{Me}_3$ at $30\text{--}35^\circ$ give 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\text{K}$, which with solid CO_2 gives only 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ but with gaseous CO_2 gives also some 5-m-*xylylmalonic acid*, softens at $149\text{--}150^\circ$, decomp. $154\text{--}155^\circ$. Addition of 2- $\text{C}_{10}\text{H}_7\text{Me}$ to PhCl and Na in C_6H_6 gives 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Na}$. HgEt_2 , Na, and PhPr^b give NaCMe_2Ph . Addition of PhMe to LiBu^a in Et_2O gives LiCH_2Ph . Mechanisms of metalation and carbonation are discussed. Dry KCH_2Ph and K residues are dangerous. R. S. C.

Phenylmercuri-derivatives of NH compounds.—See B., 1940, 642.

Quaternary ammonium salts with anions containing triphenylboron. D. L. FOWLER and C. A. KRAUS (J. Amer. Chem. Soc., 1940, 8, 1143–1144).—The prep. of the following compounds is described: $\text{NMe}_4\text{F}\cdot\text{BPh}_3$, m.p. $175\text{--}177^\circ$; $\text{NBu}^a_4\text{F}\cdot\text{BPh}_3$, m.p. $161\text{--}162^\circ$; $\text{NMe}_4\cdot\text{OH}\cdot\text{BPh}_3\cdot\text{EtOH}$, m.p. $125\text{--}130^\circ$ (decomp.); $\text{NMe}_4\cdot\text{OH}\cdot\text{BPh}_3\cdot\text{H}_2\text{O}$, m.p. $185\text{--}187^\circ$; $\text{NBu}^a_4\cdot\text{OH}\cdot\text{BPh}_3$, m.p. $143.5\text{--}145.5^\circ$. Only small ions, such as NH_2^+ , OH^+ , and F^+ , form stable complexes with BPh_3 by co-ordination; the salts are stable in air. A no. of unstable compounds have been prepared. W. R. A.

Organo-selenium compounds. II. Derivatives of phenylseleninic acid and phenylseleninamide. C. K. BANKS and C. S. HAMILTON (J. Amer. Chem. Soc., 1940, 62, 1859–1860; cf. A., 1939, II, 525).— $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SeCN}$ (I) with $\text{NH}_3\text{--H}_2\text{O--EtOH}$ gives *di-p-acetamidophenyl diselenide*, m.p. 143° (decomp.), and with Cl_2 in CHCl_3 gives *p-acetamidophenyl-selenium trichloride*, m.p. 161° (decomp.), hydrolysed by $\text{EtOH--Et}_2\text{O}$ to the *-seleninic acid*, m.p. 109° (decomp.). $\text{H}_2\text{--Raney Ni}$ at 2.67 atm. in COMe_2 reduces ($p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{Se}$) $_2$ to *di-p-aminophenyl diselenide*, m.p. 80° (decomp.), which, when dissolved in 10N- HNO_3 at -5° and then poured into $\text{NH}_3\text{--EtOH--H}_2\text{O}$, gives *p-aminophenylseleninamide* [hydrochloride, m.p. 200° (decomp.)]. By a similar reaction, (I) gives *p-acetamidophenylseleninamide*, m.p. 211° (decomp.). $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SeO}_2\text{H}$ with SOCl_2 and then aq. NH_3 gives *p-nitrophenylseleninamide*, m.p. 183° (decomp.), and with boiling, fuming HNO_3 and a trace of HCl gives *p-nitrophenylselenonic acid*, $+4\text{H}_2\text{O}$, m.p. $113\text{--}115^\circ$. Stability is determined by the substituent, decreasing in the order NO_2 , NHAc , NH_2 . R. S. C.

Organic compounds of tungsten. F. HEIN and E. NEBE (Naturwiss., 1940, 28, 93).—W hexaphenoxide reacts readily with MgPhBr giving a brown substance. Analogous compounds are obtained from

WCl_6 and Grignard reagents or LiPh . As in the case of Mo, amorphous mixtures are produced. Compounds $\text{PhWO}_{3.5}\text{H}_2$, or $(\text{PhW})_2\text{O}_7\text{H}_4$, and $\text{Ph}_3\text{W}_2\text{O}_8\text{H}_7$ have been isolated. In colour, appearance, and reactions they resemble the corresponding Mo compounds, and like them they are even less stable than the org. Cr salts. A. J. M.

Physical investigation of protein molecules.—See A., 1940, I, 350.

Wrinch's theory of protein structure. A. FODOR (Enzymologia, 1939, 6, 207–208; cf. A., 1939, II, 192).—Polemical. W. McC.

Patterson projection of the skeletons of the structure proposed for the insulin molecule.—See A., 1940, I, 350.

Fabric theory of protein structure.—See A., 1940, I, 350.

Metaphosphoric acid--protein reaction.—See A., 1940, III, 764.

Maltol from the products of hydrolysis of protein matters with hydrochloric acid. K. KIHARA (J. Soc. Chem. Ind. Japan, 1940, 43, 132B).—Maltol, obtained from soya-bean protein or crude gluten by hydrolysis (HCl), extraction with Et_2O , and purification by FeCl_3 , sublimes on heating, contains neither N nor S, reduces ammoniacal Ag, and gives a red-violet Fe^{III} and a green Cu^{II} salt. A. Li.

Gluten protein. A. G. MCCALLA and N. GRALÉN (Nature, 1940, 146, 60–61).—The behaviour of a soft wheat gluten dispersed in aq. Na salicylate on ultra-centrifuging, and the results of diffusion studies, are reported. The mols. are long and thin, but their shape differs in different fractions. There are many lengths of mols., and the theory that only two proteins, glutenin and gliadin, make up gluten must be rejected. The present results support the view that gluten protein is a protein system made up of components that vary systematically in chemical and physical properties (cf. A., 1939, III, 869). L. S. T.

Amino-acids of casein phosphopeptide. M. DAMODARAN and B. V. RAMACHANDRAN (Nature, 1940, 145, 857).—Digestion with trypsin of the ppt. of “paranuclein” obtained by the action of pepsin on casein yields a phosphopeptide of const. composition and resistant to further action of trypsin. The substance, isolated as the Ba salt, contains 10% of $\text{NH}_2\text{-N}$ and has N : P ratio 3.2–3.3, indicating a polypeptide of 10 NH_2 -acids (3 glutamic acid, 3 isoleucine, 4 serine; cf. A., 1927, 1211) united to three H_3PO_4 residues. L. S. T.

Physical chemistry of nucleoproteins. I. Preparation and general properties. R. O. CARTER and J. L. HALL (J. Amer. Chem. Soc., 1940, 62, 1194–1196).—Prep., sp. vol., n , η , and the titration curve of calf thymus nucleoprotein (N 16.73, P 4.6%) and prep. of hog thyroglobulin are described. R. S. C.

State of guanidine groupings in protein molecules. J. ROCHE and G. BLANC-JEAN (Compt. rend., 1940, 210, 681–683).—30–35% of the

guanidine radicals in clupeine, salmine, and scombrine, 50% in coregonine, sturine, thymohistone, globins, edestin, and ovalbumin, and 75% in casein, gliadin, and zein are mono-substituted (Sakaguchi reaction). Acid hydrolysis of the protein increases the proportion of guanidine radicals which give the Sakaguchi reaction to a val. $>$ that calc. from the arginine content. The theoretical val. is obtained after prolonged hydrolysis. J. L. D.

Decomposition of seleniferous proteins in alkaline solutions. E. G. PAINTER and K. W. FRANKE (J. Biol. Chem., 1940, **134**, 557—566).—The Se contents of the hydrolysates obtained after alkaline hydrolysis of seleniferous proteins and after alkali treatment of acid hydrolysates are reported. Alkaline hydrolysis in presence of PbO caused a much greater reduction in Se content. Simultaneous S determinations indicated that whilst the stability of the protein-Se was comparable with that of S, more of the Se remained in the filtrate from the Pb ppt. Acid hydrolysis, on the other hand, caused a greater loss of "labile Se" than of "labile S." A. L.

Small Buchner funnel for qualitative organic analysis. C. A. ROSWELL (Ind. Eng. Chem. [Anal.], 1940, **12**, 350).—A small porcelain plate is sealed into a portion of a Pyrex test-tube, to the bottom of which a small tube is sealed. J. D. R.

Determination of the carbon content of organic materials. Simple micro-method. B. E. CHRISTENSEN, R. WONG, and J. F. FACER (Ind. Eng. Chem. [Anal.], 1940, **12**, 364—365).—The substance is oxidised with $K_2Cr_2O_7-H_2SO_4$ and the CO_2 evolved is absorbed in standard $Ba(OH)_2$, the excess of which is back-titrated with HCl. A special apparatus is described and procedure is detailed. J. D. R.

Micro-Carius halogen and sulphur determination. J. B. NIEDERL, H. BAUM, J. S. MCCOY, and J. A. KUCK (Ind. Eng. Chem. [Anal.], 1940, **12**, 428—431).—The procedure combines the best features of earlier methods: it minimises the danger of explosions, reduces the time of heating, and eliminates contamination of the reaction product by glass splinters. The same method of filtration and apparatus are used for both halogen and S determinations. Details of manipulation are given. L. S. T.

Micro-determination of sulphur in organic compounds. Absorption apparatus for use with the combustion method. L. T. HALLETT and J. W. KUIPERS (Ind. Eng. Chem. [Anal.], 1940, **12**, 357—359).—Two forms of absorber which can be used for the determination of S by combustion are described. One is designed so that the products of combustion can be washed from the absorber without removing the tube from the furnace. SO_3 mist is eliminated from this type except with substances which burn very rapidly. The other absorber has an electro-precipitator for depositing SO_3 mist and the simultaneous formation of O_3 oxidises lower oxides of S to SO_3 . This absorber allows rapid burning, uses H_2O as absorbent, and allows direct titration of SO_4^{2-} with a tetrahydroxybenzoquinone indicator. J. D. R.

Micro-determination of sulphate obtained from combustion of organic compounds. Tetrahydroxy[benzo]quinone as an indicator. L. T. HALLETT and J. W. KUIPERS (Ind. Eng. Chem. [Anal.], 1940, **12**, 360—363).—The conditions under which tetrahydroxybenzoquinone may be used as an indicator in the determination of S, using 0.01N- $BaCl_2$, are described. If an electro-precipitator for SO_3 mist is used in the absorber, no oxidising agent need be added before titration. Without the precipitator, Br is used to oxidise SO_2 to SO_3 . The precision of the method is $\pm 0.25\%$. J. D. R.

Micro-determination of nitrogen by the hypobromite method, using copper as catalyst. I. REIFER (New Zealand J. Sci. Tech., 1940, **21**, 169—170B).—Cu can be used as catalyst in the Kjeldahl determination of N without distillation when HCl is replaced by $H_2C_2O_4$ (not citric or tartaric acid), which prevents the formation of CuI and I when KI is added. The solution (0.05—0.15 mg. of N) is digested for 30 min. with H_2SO_4 containing $CuSO_4 \cdot 5H_2O$. When cool, a mixture containing Na oxalate and borate is added, followed by aq. NaOH containing Me-red and thymol-blue. Neutralisation is completed by the addition of 27% NaOH, and KBr-Br solution is added. After addition of KI and aq. $H_2C_2O_4$, the solution is titrated with 0.01N- $Na_2S_2O_3$ (starch). The method is accurate to $\pm 1\%$, and is as good as the Parnas-Wagner distillation method. L. S. T.

Potentiometric studies in oxidation-reduction reactions. Oxidation with chloramine-T.—See A., 1940, I, 371.

Determination of unsaturation in aliphatic hydrocarbon mixtures by bromine absorption. B. LEWIS and R. B. BRADSTREET (Ind. Eng. Chem. [Anal.], 1940, **12**, 387—390).—The sample in $n-C_7H_{16}$ is treated with $KBrO_3-KBr-H_2SO_4$ and the excess of Br determined. Some S compounds (e.g., mercaptans and disulphides) affect the Br no., and catalysts (usually metal salts) have been found which minimise but do not eliminate this effect. J. D. R.

Micro-analysis of gases. Acetylene, benzene, and some procedure modifications. F. E. BLANCHET, A. L. SELLERS, and W. J. BLAEDEL (Ind. Eng. Chem. [Anal.], 1940, **12**, 356—357).— C_2H_2 is quantitatively removed from a mixture with CO and C_3H_6 by a bead of $Hg(CN)_2-KOH$; C_3H_6 may be determined in the residue by absorption in H_2SO_4 and CO by absorption on Ag_2O . C_6H_6 vapour is determined either by absorption in fuming H_2SO_4 , followed by KOH, or by absorption in aq. $NH_3-Ni(CN)_2$ followed by P_2O_5 or H_2SO_4 ; results by the two methods agree well. A detailed description is given of a new combustion coil for burning gases and a change in the method of preparing a CuO-KOH reagent for H_2 absorption is described. J. D. R.

Physico-chemical determination of components in mixtures. G. IBING (Angew. Chem., 1940, **53**, 60—65).—The proportion of an individual (A) in a mixture (B) is deduced from determinations of the apparent mol. wt. of (B) in (A) as solvent and in a second liquid which is not present in (B). Apparatus

for cryoscopic measurements at -200° to 700° is described. The method is applied to the determination of C_6H_6 and its homologues, of condensed aromatic hydrocarbons, and phenols. H. W.

Determination of certain polyalcohols in presence of each other. N. ALLEN, H. Y. CHARBONNIER, and R. M. COLEMAN (Ind. Eng. Chem. [Anal.], 1940, 12, 384—385).—With H_5IO_6 (I), glycerol (II) yields $2CH_2O$ and HCO_2H , whilst $(CH_2OH)_2$ (III) yields $2CH_2O$. (II) and (III) are determined in mixtures by oxidation with (I), followed by determination of HCO_2H [which gives the (II) content] and of HIO_3 [which gives (II) + (III)]. When a third glycol, not oxidised by (I), is present (*e.g.*, diethylene glycol), the sample is oxidised with $K_2Cr_2O_7-H_2SO_4$, from which the total glycol content is determined. (II) and (III) are determined separately, and the third glycol determined by difference. (II) may be distinguished from (III) by development of acidity by (II) on mixing with a neutralised solution of (I). A method for investigating unknown solutions of polyhydric alcohols is outlined. J. D. R.

Permanganimetric titration of formic acid and formaldehyde in alkaline solution.—See A., 1940, I, 372.

Bromometric determination of allyl compounds. F. WESSEL and M. KESZLER (Ber. ung. pharm. Ges., 1937, 13, 161—164; Chem. Zentr., 1937, i, 4136).—Diallylacetic acid is determined as follows: 0.05—0.06 g. is dissolved in 10 c.c. of MeOH or EtOH, 15 c.c. of 20% HCl and 0.5 g. of KBr are added, and the solution is titrated immediately with 0.1N-KBrO₃. Diallyl- (0.05—0.07), allylisopropyl-, and phenylallyl-barbituric acid (0.13—0.16 g.) are hydrolysed by refluxing with 5—6 c.c. of 10% NaOH for 20 min. 25 c.c. of 20% HCl are added, and the cooled solution is titrated with 0.1N-KBrO₃ to a pale yellow colour; 120—150 c.c. of H_2O , a crystal of KI, and starch are then added, and the I is back-titrated with 0.1N- $Na_2S_2O_3$. A. J. E. W.

Wijs iodine method. J. W. McCUTCHEON (Ind. Eng. Chem. [Anal.], 1940, 12, 465).—Determination of the Wijs I val. of Et linoleate and elaidate, Me linolenate, and elaidic acid gives results ~98.8% of theoretical. The reliability of the method is > is generally supposed but corrections should be applied when I val. is used as a measure of purity. J. D. R.

Modification of the Miller-Muntz method for colorimetric determination of lactic acid. R. H. KOENEMANN (J. Biol. Chem., 1940, 135, 105—109; cf. A., 1939, III, 110).—The p - $C_6H_4Ph\cdot OH$ is dissolved in a min. quantity of 0.18M-NaOH, instead of using it dry. The intensity of colour is 88% of that produced by the original method, but the accuracy is scarcely affected. A. LI.

Photographic silver-gelatin paper as reagent in drop analysis.—See B., 1940, I, 372.

Analysis of mixtures of aliphatic acids. Simultaneous qualitative and approximate quantitative determinations. S. T. SCHICKTANZ, W. I. STEELE, and A. C. BLAISDELL (Ind. Eng. Chem. [Anal.], 1940, 12, 320—324).—The acids [HCO_2H (I),

$AcOH$ (II), $EtCO_2H$ (III), Pr^iCO_2H (IV), and $PrCO_2H$ (V)] are mixed with C_6H_6 and distilled, when (I) and (II) distil as a binary mixture and are determined together by titration. C_6H_6 is removed and PhMe added; three fractions are obtained containing (III), (IV), and (V), respectively, which are determined by titration. If the acids are in the form of salts, these are dried in C_6H_6 , the acids liberated by p - $C_6H_4Me\cdot SO_3H$, and the distillation is carried out as before. J. D. R.

Determination of reducing sugar in presence of sucrose.—See A., 1940, III, 779.

Effect of certain carbohydrates on the determination of carotene. E. J. LEASE and J. H. MITCHELL (Ind. Eng. Chem. [Anal.], 1940, 12, 337—338).—Carotene (I) is incompletely extracted by EtOH-KOH from stored raw or cooked sweet potatoes and other cooked vegetables; the KOH forms a resinous film of polymerised carbohydrate which renders (I) unextractable. In samples with much carbohydrate, (I) may be determined by extraction with EtOH. If EtOH-KOH is used the material should be boiled with H_2O to dissolve resins before extraction of (I) with fat solvents. J. D. R.

Microscope hot stage for determination of m.p. [of carotene].—See A., 1940, I, 374.

Estimation of *o*-nitrophenol in *p*-nitrophenol and *o*-aminophenol in *p*-aminophenol by fluorescence analysis. W. SEAMAN, A. R. NORTON, and O. E. SUNDBERG (Ind. Eng. Chem. [Anal.], 1940, 12, 403—405).—The nitrophenol is boiled with Zn-HCl, filtered, and the filtrate adjusted to p_H 5.1 with aq. NH_3 and extracted with Et_2O . The Et_2O -sol. material is heated with BzOH to 155 — 160° and the melt dissolved in aq. NH_3 and extracted with C_6H_6 , which gives a fluorescent solution. The fluorescence is matched against known standards prepared from synthetic mixtures of pure *o*- and *p*- $NO_2\cdot C_6H_4\cdot OH$. The same procedure is applied to mixed $NH_2\cdot C_6H_4\cdot OH$, omitting the reduction stage. The fluorescence is caused by an unknown by-product in the fusion of o - $NH_2\cdot C_6H_4\cdot OH$ with BzOH. J. D. R.

Chemical and metabolic studies on phenylalanine. III. Amino-acid content of tissue-proteins of normal and phenylpyruvic oligophrenic individuals. Determination of phenylalanine. R. J. BLOCK, G. A. JERVIS, D. BOLLING, and M. WEBB (J. Biol. Chem., 1940, 134, 567—572).—Results of the determination of the phenylalanine in various proteins after hydrolysis with 8N- H_2SO_4 , HCl, HCl- HCO_2H , HI, and 5N-NaOH are reported; the highest vals. were obtained with NaOH. The N, S, histidine, arginine, lysine, cystine, tyrosine, tryptophan, threonine, and phenylalanine contents of proteins prepared from the blood sera, erythrocytes, brain, liver, and kidney of normal and phenylpyruvic oligophrenic individuals were essentially the same. A. L.

Colour reactions of bile acids.—See A., 1940, III, 743.

Micro-determination of histidine.—See A., 1940, III, 779.

Micro-determination of adenine, guanine, xanthine, and hypoxanthine in presence of uric acid. I. REIFER (New Zealand J. Sci. Tech., 1940, 21, 171—178B).—The purine solution (0.01—0.2 mg. of purine-N) is treated at room temp. with Cu_2O in presence of CuSO_4 , citrate buffer (p_{H} 5), and EtOH. The pptd. purine- Cu_2O compound (II) is centrifuged, washed, dissolved in $\text{CCl}_3\text{CO}_2\text{H}$ (I), and heated at both acid and alkaline reactions to decompose (I) and remove interfering substances. Pptn. with Cu_2O is repeated to complete the removal of uric acid, and the ppt. digested with H_2SO_4 . The resulting NH_3 is determined by the OBr' method (A., 1940, II, 318). Test data recorded show that for 0.05 mg. of purine-N the method is accurate to $\pm 1\%$. Combined purines are hydrolysed by means of 0.5N- H_2SO_4 in 7.5% HCO_2H , followed by deproteinisation with Na_2WO_4 . The presence of Cl' (cf. A., 1935, 1045) inhibits pptn. of (II). Analyses of grasses and clovers show that 5% of the total N may be purine-N. L. S. T.

Nature of the Feulgen reaction with nucleic acid. C. S. SEMMENS (Nature, 1940, 146, 130—131).—The leuco-base of fuchsin is immediately restored to its original colour by heterocyclic compounds such as $\text{C}_5\text{H}_5\text{N}$ and piperidine. Caffeine, theobromine, adenine, and guanine give magenta colours with different samples and preps. of leuco-base after varying periods of time. L. S. T.

Determination of methylated *Atropa* alkaloids. F. REIMERS (Arch. Pharm., 1940, 278, 136—142).—Methylatropine bromide (I) (0.1—0.2 g.) is kept with 2N-NaOH for 30 min., after which the solution is acidified with HCl and thrice extracted with CHCl_3 - Pr^nOH (3:1). The filtered extract is evaporated to dryness and the residual tropic acid is determined by dissolution in H_2O and titration with 0.1N-NaOH in presence of phenolphthalein (II). Alternatively (I) is dissolved in 0.1N-NaOH the excess of which is determined after 30—60 min. by titration with 0.1N-HCl in presence of (II). The second method is applicable to methylhomatropine bromide. The first method also can be used if Et_2O replaces CHCl_3 - Pr^nOH ; during evaporation of the latter small amounts of OH-CHPh-CO $_2\text{H}$ are volatilised. H. W.

Titration of morphine. W. POETHKE (Arch. Pharm., 1940, 278, 109—125).—The indicator correction is very small when morphine (I) is titrated with Me-red (II) to p_{H} 5.0 but it cannot be neglected and a comparison solution is recommended for exact results. The error caused by increase in vol. is small when, in accordance with the Swiss Pharmacopœia V, dilution to an EtOH content of $\sim 25\%$ is made since the end-point of (II) is well-defined in 25% EtOH. With MeOH dilution to 40% suffices since under these conditions a sharp end-point is obtained with a comparison solution; with EtOH dilution to 25% content is essential. In 50% EtOH the correction is very small when (I) is titrated with bromophenol-blue as indicator but a comparison solution is advisable. In more dil. EtOH or in H_2O accurate results are obtained only by use of a correction. Acid com-

bined with narcotine (III) cannot be titrated accurately with (II) as indicator. When excess of acid in a solution containing (I) and (III) is titrated in presence of (II) the latter has a pure red colour at the equivalence point of the salt of (III). In the determination of pure (I) titration must be effected to p_{H} 5 (yellow-red) and this shade can be detected readily in presence of (III). The acid consumption is smaller, particularly in presence of MeOH, than that required for (I) + (III) but considerably greater than for (I) alone. If only traces of (III) are present as in impure (I), almost exactly (I) + (III) is found at p_{H} 5 but a sharp end-point is not obtained if it is attempted to determine acid combined with (III) by further addition of alkali. Any yellow colour persists so long as (III) remains in supersaturated solution and the solution becomes yellow-red or red when (III) separates. Pure (I) must be finally determined; the effect of contamination with (III) cannot be excluded in the titration. H. W.

Electrolytic [micro-]method for the determination of the basic amino-acids in proteins. A. A. ALBANESE (J. Biol. Chem., 1940, 134, 467—482).—The protein is boiled with 20% HCl, and a portion of the hydrolysate (≈ 0.5 —1 g. of protein) is electrolysed by a modification of the three-compartment cell method of Foster and Schmidt (A., 1923, i, 963). A first electrolysis eliminates HCl and more acidic NH_2 -acids; the contents of the cathode compartment are brought to p_{H} 5.6—5.8 and re-electrolysed. From the resulting cathodic electrolyte, arginine is pptd. as flavianate (I), and excess of flavianic acid removed electrolytically. Histidine (II) is determined by pptn. (centrifuge) with HgCl_2 at p_{H} 7 (cf. Foster *et al.*, Organic Syntheses, 1938, 18, 43). Total N of the washings [corr. for solubility of (I)] determines lysine (III). The purity of (I), and the absence of disturbing factors in the determination of (II) and (III), are established. Analyses of gelatin, cattle fibrin, casein, and horse hæmoglobin by this method are tabulated; results are reproducible within much narrower limits than in previous methods. E. W. W.

Determination of proline in mixtures containing *l*- and *dl*-proline. Proline content of gelatin. W. H. STEIN and M. BERGMANN (J. Biol. Chem., 1940, 134, 627—633).—In the method previously described (A., 1939, II, 236), a solution containing *l*- (I) and *dl*-proline (1:1) ppts. a *dl*-rhodanilate (II) which is considerably less sol. in aq. MeOH than is *l*-proline rhodanilate (III). A mixture of (I) and *dl*-proline (IV) ppts. a mixture of rhodanilates in which the original proportions are approx. preserved; (II) and (III) form solid solutions, as is also shown by solubility measurements. Total proline is determined as rhodanilate, and the proportions of (I) and (IV) polarimetrically. Applied to hydrolysates, the method shows that gelatin and tendon collagen contain 17.5 (± 0.5)% of proline, and that *d*-proline is $\approx 1.5\%$ of total proline. During prolonged hydrolysis of gelatin with boiling HCl, appreciable racemisation of (I) occurs, but (unless some is lost in the first, peptide, stage) no appreciable destruction. E. W. W.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1940.

Substitution, addition, and elimination. W. HÜCKEL (Angew. Chem., 1940, 53, 49—54).—A lecture. H. W.

Preparation and some physical properties of $\beta\beta\delta\delta$ -tetramethylpentane. F. L. HOWARD (J. Res. Nat. Bur. Stand., 1940, 24, 677—684).—The method of Whitmore and Southgate (A., 1939, II, 1) for prep. of $\beta\beta\delta\delta$ -tetramethylpentane has been improved and the following consts. among others are given: m.p. —66–600°; b.p. 122–281°/760 mm. W. R. A.

Mechanism of substitution at a saturated carbon atom. XI—XXV.—See A., 1940, I, 391.

Kinetics of olefine elimination from ethyl, isopropyl, *tert.*-butyl, and α - and β -phenylethyl bromides in acidic and in alkaline alcoholic solution.—See A., 1940, I, 390.

Influence of substitution on organic bond strength. E. T. BUTLER and M. POLANYI (Nature, 1940, 146, 129).—The breaking of C—I in various org. iodides has been studied by passing the vapour of the iodide at 0.01 mm. pressure diluted with N_2 or H_2 at 6 mm. through a tube at 300—500°, and analysing the products for I and HI. The vals. recorded show partial double linking character in vinyl and Ph iodides, and in benzyl, allyl, and acetyl iodides indicate the degeneracy of the free radical resulting from conjugation of the unshared electron with the double linking or the C_6H_6 ring. Bu^*I shows a strong reduction in linking strength. L. S. T.

Solvent and peroxide effect in the addition of hydrogen bromide to unsaturated compounds. IV. ***iso*Propylethylene.** A. MICHAEL and N. WEINER (J. Org. Chem., 1940, 5, 389—400).—The appearance of a rearrangement product in the addition of conc. aq. HBr to $CHPr^{\delta}:CH_2$ is confirmed. In the presence of air the yield of *sec.* bromide (I) amounts to 49% and that of *tert.* bromide (II) to ~51% of the theoretical. Ascaridole (III) induces the formation of the abnormal primary bromide (IV) formed at the expense of (I). In the absence of solvent dry HBr adds to $CHPr^{\delta}:CH_2$ (V) to yield more (II) and less (I); H_2O , therefore, shows a solvent effect, and the conclusion that dry HBr and aq. HBr furnish identical additive compounds in the same proportion can no longer be upheld. In additive reactions HBr probably functions as the hydrated form. The change in the course of addition may be explained by an approach in the relative positivities of the unsaturated C atoms in (V) due to the multimol. union of the hydrated acid to a greater extent at the relatively positive methinyl C. With dry HBr (III) induces

the formation of (IV) mainly at the expense of (I) up to 0.009 mol. concn. but a further increase involves (II) which at 0.02 mol. concn. almost disappears. The unusual fall in reaction velocity, previously observed with $CHMe:CMe_2$ in MeOH, is met with in (V). No addition occurs at —78° or at 0° in MeOH alone or at higher temp. in presence of (III). However, at —78° a certain crit. concn. of (III) induces addition and >80% of (IV) appears; further increase in concn. is ineffective in altering the relative proportion of the products. Et_2O exerts a marked solvent effect leading to the formation of ~53% of (IV) at the expense of (I) and (II). Contrary to general results $NHPh_2$ is more effective than quinol (VI) in reducing abnormal addition to (V) but the influence of these antioxidants is much less with (V) than with most Δ^a -alkenes. AcOH in a vac. or in the presence of antioxidants causes the appearance of 44—47% of (IV); small amounts of (III) decidedly augment the proportion of (IV), which decreases slightly in amount with increasing concn. of (III). With $CHCl_2 \cdot CO_2H$ a much smaller proportion of (IV) is obtained. Compared with the result of solvent-free addition of HBr to the hydrocarbon, the amount of (II) is only slightly diminished whilst that of (I) declines considerably. In comparison with the influence of AcOH drastic changes occur; the % of (I) is slightly decreased but that of (IV) diminishes by > half whilst that of (II) is > doubled. The result is independent of the presence of (VI). (III) (0.05—0.005M.) reduces the yield of (II) and increases that of (IV) but comparatively \ll in AcOH. In the presence of $CCl_3 \cdot CO_2H$ addition becomes normal in the sense that only (I) and (II) are formed. The presence of this strong acid increases the formation of (II) at the expense of (I). The same result is obtained in presence of (VI). The formation of (II) by the action of HBr on (V) should not be considered an abnormal addition. It is a normal consequence of the affinity and energy relationships existing in the chemical system. The chemical behaviour of this system manifests itself, alone and in the presence of solvents, oxidants, and antioxidants, by changes peculiar to the hydrocarbon. H. W.

Preparation of methyl chloride from natural gas.—See B., 1940, 591.

Catalytic reactions of carbon monoxide and hydrogen at high pressure. I. Synthesis of isobutyl alcohol.—See B., 1940, 591.

Molecular size in ethylene oxide polymerides. P. J. FLORY (J. Amer. Chem. Soc., 1940, 62, 1561—1565).—In polymerides formed by the addition of

monomerides to a fixed no. of polymeride mols., e.g., the condensation products of $(\text{CH}_2)_2\text{O}$ with $(\text{CH}_2\text{OH})_2$, the proportions of the mols. of various sizes are represented by Poisson's distribution law. Equations representing these proportions are derived and curves are given showing the calc. proportions in polymerides of average size 6—500 units. Such polymerides are much more homogeneous than condensation polymerides.

J. W. S.

Synthesis of isopropyl ether. Direct hydration of propylene to isopropyl ether and alcohol.—See B., 1940, 591.

Synthesis of $d(+)$ - α -glycerophosphoric acid and action of phosphatases on synthetic $d(+)$ -, $l(-)$ -, and dl - α -glycerophosphoric acids. E. BAER and H. O. L. FISCHER (J. Biol. Chem., 1940, 135, 321—328; cf. A., 1939, II, 296).— $d(+)$ - α -Glycerophosphoric acid [Ba and Ag salts; Et_2 ether Et_2 ester, b.p. 104—105°/0.22 mm., $[\alpha]_D^{20} +5.94^\circ$ (homogeneous), $+6.69^\circ$ in EtOH] has been synthesised from $l(-)$ -diisopropylideneglycerol. It is hydrolysed more rapidly than the $l(-)$ -acid by kidney, rat bone, and taka-phosphatases, and phosphatase from dog faeces. Muscle press-juice hydrolyses the $l(-)$ -acid completely, and does not affect the $d(+)$ -acid (Meyerhof).

A. LI.

Xanthates. II. Sodium ethylthioxanthate and its reactions with metals. III. Mechanism of xanthation. K. ATSUKI and T. TAKATA (J. Cellulose Inst. Tokyo, 1940, 16, 161—162, 163—169; cf. A., 1939, II, 532).—II. Na ethylthioxanthate, m.p. 88.1—88.3°, has been prepared by adding NaOH to cold EtSH, adding CS_2 , and crystallising from EtOH and Et_2O after removal of excess of CS_2 . Its composition is established by analysis and by its reactions with metallic salts.

III. Xanthation occurs by the characteristic and selective affinity of the S atom in CS_2 for metallic atoms or groups. Xanthic and dithiocarbonic acids are not intermediate compounds. In the xanthation of cellulose spatial arrangements usually prevent >1 OH group per C_{12} unit from reacting, but if the cellulose is dissolved in NEt_4OH xanthation may occur at all the OH groups.

W. A. R.

Resonance in the chloroacetic acids.—See A., 1940, I, 386.

Reaction of sodium in liquid ammonia with esters. M. S. KHARASCH, E. STERNFELD, and F. R. MAYO (J. Org. Chem., 1940, 5, 362—378; cf. A., 1939, II, 97).—The action of one or two equivs. of Na on an ester gives respectively a free radical and a very reactive organo-Na compound. Similar compounds can be obtained by the combined action of NaNH_2 and NaOEt on a diketone or an acyloin. Only 0.5 mol. of EtOAc, EtCO_2Et , $\text{Pr}^i\text{CO}_2\text{Et}$, $\text{Bu}^i\text{CO}_2\text{Et}$, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$, $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$, or EtOBz is required to discharge the colour of a solution of Na in liquid NH_3 . H_2 is not evolved during the action of the esters with one or two mols. of Na or when the reaction mixture is treated with NH_4Br regardless of the presence or absence of C_6H_6 as solvent for the ester. CO is therefore attacked directly and without preliminary enolisation. In some instances considerable

reduction of ester to alcohol occurs, accompanied by approx. equiv. quantities of acid and amide. Experiments with esters in the absence of Na but in presence and absence of NaNH_2 show that the formation of amide is not due to ammonolysis of the ester. The processes of formation of alcohol and amide are related and probably due to the disproportionation of an intermediate. With one equiv. of Na EtOAc gives little Ac_2 whereas $(\text{COEt})_2$ is more readily obtained from EtCO_2Et . EtOBz gives a dark purple colour and the product is hydrolysed to Bz_2 or a mixture of Bz_2 and $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$. The probability that $\text{ONa}\cdot\text{CPh}\cdot\text{OEt}$ exists in equilibrium with its dimeride is supported by the observation that the colour of the solution is altered by O_2 and the product gives BzOH and an explosive tar. With two equivs. of Na acetoin, best isolated as the acetate, is obtained from EtOAc but the formation of pure $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ could not be confirmed, $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ being obtained in its place. EtCO_2Et behaves similarly but gives no evidence of a Claisen condensation. $\text{Pr}^i\text{CO}_2\text{Et}$ gives a derivative spontaneously inflammable in air and hydrolysed to Pr^iCHO , thus suggesting the structure $\text{OEt}\cdot\text{CPr}^i\text{Na}\cdot\text{ONa}$, which is supported by the production of COEtPr^i when the compound reacts with EtBr. $\text{Bu}^i\text{CO}_2\text{Et}$ behaves similarly; $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ gives some $\text{CH}_2\text{Ph}\cdot\text{CHO}$, but the corresponding acyloin could not be isolated. $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$ gives a very marked yellow colour but instead of $\text{CHPh}_2\cdot\text{CHO}$ gives COPh , and a greater proportion of alcohol ($\text{CHPh}_2\cdot\text{CH}_2\cdot\text{OH}$) than any of the other esters. The following appear new: propionin-2:4-dinitrophenylhydrazones, m.p. 154°; dipropionyl-2:4-dinitrophenylhydrazones, m.p. 145—145.5°; Bu^i 3:5-dinitrobenzoate, m.p. 63—64°; isobutyroinoxime, m.p. 109°; Et Pr^i ketone 2:4-dinitrophenylhydrazones, m.p. 168—169°; Et Bu^i ketone 2:4-dinitrophenylhydrazones, m.p. 175°; $\beta\beta$ -diphenylethanol, m.p. 64—65°; tetraphenylacetoin; isobenzamarone, m.p. 179°; 2:4-dinitrophenylhydrazones of valerophenone, m.p. 154°.

H. W.

Preparation of acetyl chloride without the use of phosphorus chlorides.—See B., 1940, 591.

Effect of reduced nickel on the addition of hydrogen bromide to undecenoic acid in various solvents. M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1940, 15, 113—115).—The effect of reduced Ni in reversing the mode of addition of HBr to undecenoic acid (cf. A., 1938, I, 406; II, 216, 428) is similar in C_6H_6 , CCl_4 , and ligroin to that in PhMe. In AcOH and Et_2O the effect is very slight, and the Ni is attacked. In CHCl_3 the effect is intermediate.

F. J. G.

Influence of aldehydes and hydroxyaldehydes on the addition of hydrogen bromide to undecenoic acid in presence and in absence of oxygen or reduced nickel. M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1940, 15, 116—118; cf. preceding abstract).—Pyrocatechol and quinol markedly inhibit the effects of O_2 and of reduced Ni in reversing the mode of addition of HBr to undecenoic acid in C_6H_6 . Protocatechualdehyde and vanillin have smaller, and PhCHO and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ have negligible, effects.

F. J. G.

Oxidation of drying oils and cognate substances. VI. Properties of the ketol, peroxide, and oxido-grouping, including those of some resins. R. S. MORRELL and E. O. PHILLIPS (J.S.C.I., 1940, 59, 144—148; cf. B., 1939, 625).—The reactive O vals. of polyhydric alcohols are variable. In the case of benzoin the reaction proceeds normally, but with glycerol the val. is negligible and in the case of $(\text{CH}_2\cdot\text{OH})_2$ 25% reactions occurs. In the dihydroxystearic acids (*cis* and *trans*) 60% and 20% reaction, respectively, takes place. The evidence is not yet sufficient to indicate a preferential *cis*-reaction. Colophony on oxidation in air behaves like a drying oil. In blonde shellac the presence of a ketol grouping is indicated. The enolisation of the ketol grouping has been studied with reference to the variability of the I vals. obtained by the Hübl and Wijs methods, the isomeric ketol-stearic acids showing 64—99% enolisation. The oxido-group in oxidoelaidic acid is not reduced by H_2 /atm. pressure with a Pt catalyst. It gives a hydrobromide and when heated at 100° it polymerises to a dimeride. The structural formulæ for the light petroleum-sol. and -insol. products of the methylated β -elæostearin oxyn are given: They are mixtures of oxido-methoxy-methyl esters of β -elæostearic acid. Earlier conclusions (B., 1931, 549) have been modified, confirmed, and extended.

Pectic acid. S. ÔNO (Bull. Sch. Agric., Taihoka, 1940, I, 1—39).—The isolation of pectins by extraction with boiling H_2O and addition of CuSO_4 to the extracts is described. These are snow-white in colour and both galacturonic and OMe contents are very high in comparison with those of pectins isolated previously from plant materials of the same species. They are considered to be a polymeride of trimethyl-tetragalacturonic acid containing no araban or galactan polysaccharide residues. Decomp. of Me ester groups does not occur in boiling 0.5% $(\text{NH}_4)_2\text{C}_2\text{O}_4$. So-called "insol. pectins" are derived from the insol. portions of Tûso pith and sliced radishes by use of 0.5% $(\text{NH}_4)_2\text{C}_2\text{O}_4$; they are very sparingly sol. in H_2O but their precipitability with EtOH and other reagents is identical with that of sol. pectins. The basal constituents of these pectins are the insol. mineral salts of pectic acid (I) in the plant minerals although the preps. contain a small amount of Me ester groups. They are incapable of gelling. Pectins are readily hydrolysed by dil. alkali to (I) and MeOH. (I), $[\alpha]_D +280^\circ$ and -295° , is $(\text{C}_5\text{H}_7\text{O}_4\cdot\text{CO}_2\text{H})_n$ containing no polysaccharide residue. It is generally sol. in H_2O but a kind of (I), considered as insol. pectin, is sparingly sol. It does not form a jelly. With boiling HCl (*d* 1.06) CO_2 is quantitatively evolved but the yield of furfuraldehydephloroglucide is not quant., 1 part of it corresponding with 2.73—2.74 parts of (I). (I) is also obtained from the coagulated extracts of Aigyokusi seeds by the action of pectase; apparently the enzyme causes hydrolysis which is followed by pptn. of Ca pectate, which is insol. in H_2O . Ag, Cu, Fe, Mg, Na, and Ca pectates are described; all of them, excepting the Na salt, are insol. in H_2O . The Ag salt is very photosensitive. The Fe salt carries down much Fe with the gel and the metal content is not const. so that salt formation

is not simple. In general desiccation is incomplete at 110°. The ash content is not const. but the general composition appears to be $(\text{C}_5\text{H}_7\text{O}_4\cdot\text{CO}_2\text{M})_n$. Treatment of the Ag salt with MeI under somewhat increased pressure gives Me pectate with appearance and $[\alpha]_D$ resembling those of the natural sol. pectins but the product is more freely sol. in H_2O and gives a ppt. with $\text{Pb}(\text{OAc})_2$. The OMe content is somewhat higher, but free CO_2H which can be titrated directly with alkali is present. A modification of Carré and Haynes' method for determining (I) is described and used for the determination of (I) in certain fruits. Boiling with dil. H_2SO_4 under pressure hydrolyses "sol. pectin" to a clear solution from which pectolic acid (II) is pptd. and *d*-galacturonic acid (III) is finally obtained. Insol. pectin is not dissolved by boiling dil. H_2SO_4 and (II) is not pptd. but the reducing power of the resulting mixture increases gradually with formation of (III) which can be isolated in fine, needle-shaped crystals. (III) forms a monohydrate which does not lose H_2O completely at 80°/vac. in 10 hr. The phenylhydrazone, *p*-bromo- and *p*-nitro-phenylhydrazone of (III) have m.p. 138.5°, 154°, and 180.5—181°, respectively, (lit. 134°, 152—153°, and 170—175°). H. W.

Pectin. V. Organic base derivatives of pectinic and pectic acids. R. F. STUEWER and A. G. OLSEN (J. Amer. Pharm. Assoc., 1940, 29, 303—306).—The combined cations in pectin preps. are readily removed by washing with EtOH-acid to give "pectinic acid" (1% solution has $p_H < 3$) which has an equiv. wt. (400—1200) > that of pectic acid (~205). Titration curves for pectins are given. The pectates and pectinates of various org. bases have been prepared [prep. of $\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3$ pectinate and NH_2Pr^a and methylglucamine pectates is described; the last two are sol. in 60 and 75% alcohol, respectively]. F. O. H.

Acetylformoin. I. Preparation. R. NODZU and S. KUNITIKA (Bull. Chem. Soc. Japan, 1940, 15, 211—214).—AcCHO with KCN (but not with K_2CO_3) at 0° and p_H 7.3 yields acetylformoin, m.p. 82°, which reduces cold Fehling's solution, gives with FeCl_3 a greenish-blue colour which fades on shaking, rapidly darkens and liquefies in the air, and is oxidised (KMnO_4) quantitatively to AcOH. The significance of its formation is discussed. $\text{OH}\cdot\text{CHBz}\cdot\text{COBz}$ is oxidised quantitatively to BzOH. A. LI.

Action of weak alkalis on glucose. II. R. NODZU and R. GORO (Bull. Chem. Soc. Japan, 1940, 15, 209—211; cf. A., 1936, 1094).—When distilled with dil. Na_2CO_3 , AcCHO yields no acetol (I), and $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CHO}$ only a trace; both yield Ac_2 and (in the residue) $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. Addition of AcCHO to glucose does not increase the yield of (I), which with Na_2CO_3 gives only a trace of Ac_2 . A. LI.

Structure of γ -sugars. IV. Preparation of 6-methylfructose. F. HARTLEY and W. H. LINNELL (Quart. J. Pharm., 1940, 13, 150—161; cf. A., 1939, II, 142).—1 : 2-*iso*Propyrideneglucose borate, m.p. (indef.) 90—115° (cf. von Vargha, A., 1933, 596), and 6-acetate, m.p. 145° (cf. Bell, A., 1936, 968), and 3 : 5-benzylidene-1 : 2-*isopropylideneglucose* 6-acet-

ate (I); m.p. 125—126° (cf. Bell, *ibid.*), were prepared. Simultaneous deacetylation and methylation of (I) by 30% NaOH and Me₂SO₄ in COMe₂ at the b.p. yielded the corresponding 6-Me derivative, m.p. 96°, hydrolysed (0.5N-H₂SO₄ in 50% EtOH at 100°) to 6-methylglucose (pale yellow syrup; reaction velocity const. of mutarotation, $K = 0.0122$), the phenyl-osazone, m.p. 184°, of which was converted into the corresponding glucosone (II) by hydrolysis with HCl but not by treatment with PhCHO, CH₂O, or piperonal. Reduction (Zn-AcOH) of (II) yielded 6-methylfructose (III) as a dark brown syrup, $[\alpha]_D^{25} + 17.15^\circ$ (no change in $[\alpha]$ in 3 hr.) (phenyl-osazone, m.p. 184°), which with HCl-MeOH afforded 6-methyl- γ -methylfructoside, $[\alpha]_D^{25} + 25.05^\circ$. The evidence for the structure of the isomerides of methylglucose is reviewed and the non-pyranose structure of (III) is discussed. F. O. H.

N-Glucosides. II. N-Glucosides of aniline derivatives and anilides of various sugars. K. HANAOKA (J. Biochem. Japan, 1940, 31, 95—107; cf. A., 1938, II, 394).—The influence of the carbohydrate and aglucone on the rate of hydrolysis by acids of glucosides of various derivatives of NH₂Ph was studied. Introduction of OH, OMe, OEt, or Me decreases, and that of Cl or CO₂H increases, the stability of the glucoside linking. Susceptibility to hydrolysis gives the increasing order: lactoside, maltoside for disaccharides, glucoside, mannoside, galactoside for hexoses, and *l*-rhamnoside, *d*-arabinoside, *l*-arabinoside, *d*-xyloside for pentoses; with anilinomethylglucosides, the susceptibility decreases with approach of Me to C₁, of the glucose mol. and with increase in no. of Me groups. The following were prepared: *o*-, m.p. 137°, and *p*-chloroanilino-, m.p. 126°, *o*-carbethoxyanilino-, m.p. 137°, *p*-carboxyanilino-, m.p. 127°, and α -naphthylamino-glucoside, m.p. 92°; anilino-2-, m.p. 161°, and 6-methylglucoside, m.p. 130°; anilino-*d*-arabinoside, m.p. 130°; piperidino-mannoside, m.p. 116—117°, -galactoside, m.p. 129°, -tetramethylglucoside, m.p. 74°, and -*d*-arabinoside, m.p. 103—104° (all m.p. uncorr.); data for solubility and $[\alpha]$ before and after mutarotation are given. F. O. H.

α -Phenyl-*d*-lyxoside, m.p. 178—181°, $[\alpha]_D^{25} + 123^\circ$ in H₂O.—See A., 1940, III, 766.

Constitution of the tetrasaccharide fission product of starch by *Bacillus mesentericus vulgatus* amylase. I. S. AKIYA (J. Pharm. Soc. Japan, 1938, 58, 40—45).—Hydrolysis of potato starch at 36° by the bacillus named gives a tetrasaccharide, $[\alpha]_D^{25} + 168^\circ$ in H₂O [*dodeca-acetate* (I)], hydrolysed by 2% HCl to glucose (98.3% isolated as phenyl-osazone). Methylation (Me₂SO₄-NaOH-COMe₂) of (I) and subsequent hydrolysis gives tri-, di-, b.p. 105—110°/0.002 mm., and mono-methylmethylglucosides. Methylation of (II) by MeI-Ag₂O and Br-oxidation of the product gives tetramethyl- δ -gluconolactone. HNO₃ (*d* 1.42) oxidises (II) to H₂C₂O₄ and *d*-(OMe·CH·CO₂H)₂. (II) is thus a 2:3-dimethylpyranoside. R. S. C.

Origin and composition of hemicelluloses obtained from hardwoods. E. ANDERSON, M. SEELEY, W. T. STEWART, J. C. REDD, and D.

WESTERBEKE (J. Biol. Chem., 1940, 135, 189—198).—The prep. and properties of hemicelluloses from lemon wood (I), the sap-wood (II) and heart-wood of black locust, and white birch wood, before and after chlorination of the wood, are described. (I) and (II) contain starch, and hemicelluloses therefrom give blue or pink colours with I. This property is not removed by digesting for 24 hr. with saliva or taka-diastase, whereas a mixture of starch-free hemicellulose with maize starch after similar treatment gives no colour with I. Hydrolysis (dil. H₂SO₄) of hemicelluloses from (I) gives monomethoxyuronic acids combined with 1 and 2 xylan groups (Ba salts, $[\alpha]_D^{25} + 75^\circ$ and $+65.16^\circ$ respectively), whilst those from (II) give only the former (Ca salt, $[\alpha]_D^{25} + 70^\circ$). All give *d*-xylose, but those from (I) and (II) before chlorination yield a little *d*-glucose as well. It appears that the hemicelluloses not coloured by I consist of monomethyluronic acid combined with 8—19 xylan groups, whilst those which colour I contain anhydroglucose groups in the xylan chain, and may be intermediate products in the formation of hemicelluloses from starch or dextrin. A. LI.

Reversible formation of starch from glucose 1-phosphate.—See A., 1940, III, 826.

Animal lipins. XVI. Occurrence of sphingomyelin as a mixture of sphingomyelin fatty acid ester and free sphingomyelin, demonstrated by enzymatic hydrolysis and mild saponification. XVII. Synthesis of lignoceryl sphingosine fatty acid esters (sphingosine fats) and sphingosine amides (ceramides). S. J. THANNHAUSER and M. REICHEL (J. Biol. Chem., 1940, 135, 1—13, 15—21; cf. A., 1938, III, 739).—XVI. Hydrolysis of spleen sphingomyelin (I) with liver phosphatase (in glycine buffer, *p*_H 8.9, containing MgSO₄ and a little PhMe) yields choline, H₃PO₄, cholinephosphoric acid (indicated by the difference between free and total choline), palmitic acid (II), lignoceryl sphingosine (a "ceramide"), and some unhydrolysed ester (III). With pancreatic lipase (pptd. from glycerol extracts with COMe₂), or with KOH in MeOH—light petroleum at room temp., (I) yields (II) and lignoceryl sphingosine cholinephosphoric acid (IV) [*Reinecke salt* (equimol. proportions)]. Since the CO·NH linking of ceramides is not split by the last two methods, it is concluded that (I) consists of (IV) and its *O*-palmitic ester (III). Acetylation with keten and hydrolysis of the product shows that 67.5% of (I) is esterified.

XVII. Lignoceryl sphingosine yields with keten in CHCl₃ in presence of MeOH-KOH, *OO'*-diacetyl-, m.p. 70—71°, and with the appropriate acid chloride (2 mols.) in Et₂O-quinoline, *OO'*-di-benzoyl-, m.p. 57—58°, -palmityl-, m.p. 39—40°, and -stearyl-lignoceryl sphingosine, m.p. 45—47°. These resemble triglycerides in chemical and physical properties. Sphingosine with 2 mols. of acid chloride yields tri-benzoyl-, m.p. 118—120°, -palmityl-, m.p. 67—69°, and -stearyl sphingosine, m.p. 72—74°. The last two are hydrolysed (MeOH-KOH in presence of Et₂O) to *N*-palmityl-, m.p. 86—87°, and -stearyl sphingosine, m.p. 88—89°, respectively. A. LI.

Stability of hydrogen-carbon linkings in glutamic acid. S. RATNER, D. RITTENBERG, and

R. SCHOENHEIMER (J. Biol. Chem., 1940, 135, 357—358; cf. Foster *et al.*, A., 1938, III, 1032).—Catalytic treatment of α -ketoglutaric acid with D_2 in presence of NH_3 yields glutamic acid from which no D is removed on prolonged boiling with 20% HCl. Such treatment does not introduce D into ordinary glutamic acid. Hence $H_{(g)}$ is stable. The synthetic acid (15.5 at.-% D) with chloroamine-*T* gives Ba succinate containing 28.4 at.-% D, showing that the H on $C_{(a)}$ contains 25 at.-% D. A. Li.

Racemisation of glutamic acid by heat. L. E. ARNOW and (Miss) J. C. OPSALL (J. Biol. Chem., 1940, 134, 649—651).—*l*(+)-Glutamic acid (20—500 g.) kept at 190—195° (3 hr. or more, according to quantity) gives, with 20% HCl at the b.p. (4 hr.), the hydrochloride of *dl*-glutamic acid (70% overall yield). *dl*-Pyrrolidonecarboxylic acid is formed intermediately (cf. Abderhalden *et al.*, A., 1910, i, 768).

E. W. W.

Amino-acid analogues of pantothenic acid. H. H. WEINSTOCK, E. L. MAY, A. ARNOLD, and D. PRICE (J. Biol. Chem., 1940, 135, 343—344; cf. A., 1940, III, 751).—The condensation products of $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CO_2H$ with Et_2 *l*-aspartate (b.p. 123—125°), *dl*- α -alanine Et ester (picrate, m.p. 171°), *dl*-lysine Me ester (hydrochloride, m.p. 219°), and Et β -aminobutyrate (picrate, m.p. 148.5—149°) show no biological activity in concns. up to 6.0 μ g. per c.c. of medium. Asparagine with CH_2N_2 yields a substance (? betaine) having a hydrochloride of m.p. 183°. A. Li.

Acetylation of cysteine by keten. J. J. PEREZ and G. SANDOR (Bull. Soc. Chim. biol., 1940, 22, 149—152).—That the substance obtained by Neuberger (A., 1938, II, 397) by the action of keten on cysteine is *NS*-diacetylcysteine is confirmed by its failure to decolorise porphyrindine and by the liberation of 2 mols. of AcOH on hydrolysis. A. L.

Silico-organic compounds. II. Reactions of silico-ortho-esters with certain acid anhydrides. H. W. POST and C. H. HOFRICHTER, jun. (J. Org. Chem., 1940, 5, 443—448).—The reaction between silico-ortho-esters and acid anhydrides follows a mechanism which can be explained on the assumption of an ionic splitting: $SiEt(OR)_3 \rightleftharpoons SiEt(OR)_2^+ + (OR)^-$; $Ac_2O \rightleftharpoons AcO^- + Ac^+$; $SiEt(OR)_2^+ + AcO^- \rightleftharpoons OAc\cdot SiEt(OEt)_2$; $Ac^+ + OR' \rightleftharpoons ROAc$. The monoacylated compound, once formed, may dissociate in two different ways: $OAc\cdot Si(OEt)_3$ (I) $\rightleftharpoons OAc\cdot Si(OEt)_2^+ + OEt$ and $OAc\cdot Si(OEt)_2 + OAc^- \rightleftharpoons (OAc)_2Si(OEt)_2$ or (I) $\rightleftharpoons Ac^+ + [OSi(OEt)_3]^-$ (III) and (II) + (III) \rightarrow products of high mol. wt. Determination of the sp. reaction velocity coeff. at the refluxing temp. of the mixture of Pr ethaneortho-siliconate and Ac_2O shows that the acetylation reaction is most probably of the second order; this fact is in agreement with an ionic mechanism such as is postulated. Propionylation probably follows the same mechanism. In the fractionation of the product obtained from the reaction between $Si(OEt)_4$ and Bz_2O the reaction is forced to the left since $Si(OEt)_4$ is the fraction of lowest b.p. For this reason a pure compound could not be isolated. The following appear new: *diethoxyethylsilicomethyl acetate*,

$OAc\cdot SiEt(OEt)_2$, b.p. 94°/15 mm., 191.5°/atm. pressure; *triethoxysilicomethyl acetate*, b.p. 81°/19 mm.; *diethoxysilicomethyl diacetate*, b.p. 100°/19 mm.; *triethoxysilicomethyl propionate*, b.p. 101°/15 mm.; *diethoxysilicomethyl dipropionate*, b.p. 125°/15 mm.

H. W.

Organic compounds of tantalum. B. N. AFANASIEV (Chem. and Ind., 1940, 631—633).—The action of $MgPhBr$ on $TaCl_5$ gives small amounts of an exceedingly unstable organo-metallic compound which is readily oxidised by air and converted by H_2O into Ta_2O_5 . A still less stable compound is produced from $TaCl_5$ and $MgEtBr$, thus supporting von Grosse's theory of the instability of org. derivatives of elements in the atoms of which the valency electrons do not possess the same main quantum no. H. W.

Preparation of mercury diethyl.—See B., 1940, 591.

Combustion of aromatic and alicyclic hydrocarbons. V. Products of combustion of benzene and its monoalkyl derivatives. J. H. BURGOYNE (Proc. Roy. Soc., 1940, A, 175, 539—563).—Analytical study of the products of combustion of C_6H_6 , $PhMe$, $PhEt$, $PhPr$, and of a cool-flame reaction of the last, shows that the reaction consists of degradation of the side-chain (if present) and rupture of the C_6H_6 nucleus, followed by rapid degradation of the higher aliphatic aldehyde thus formed, yielding CH_2O and ultimately CO_2 , CO , and H_2O . G. D. P.

Representation of the benzene ring. G. N. COPLEY (Chem. and Ind., 1940, 626).—A discussion of methods of writing formulæ for C_6H_6 , $C_{10}H_8$, anthracene, and phenanthrene.

Chlorination of toluene in presence of water.—See B., 1940, 591.

Allenes. III. Comparison of some substituted allenes with pyrethron with respect to their behaviour towards halogens. F. ACREE, jun., and F. B. LAFORGE (J. Org. Chem., 1940, 5, 430—438).—Addition of Br ($\equiv 2$ atoms) to $CHPh\cdot C\cdot CHMe$ in CS_2 in presence of aq. Na_2SO_4 gives almost exclusively $\beta\gamma$ -*dibromo- α -phenyl- Δ^2 -butene*, b.p. 118°/0.5 mm. [the structure of which is proved by its conversion by aq. KOH at 100° into (probably) γ -*bromo- α -phenyl- Δ^2 -butadiene*, b.p. 84—89°/0.5 mm.], β -*bromo- α -phenyl- Δ^2 -buten- γ -ol*, b.p. 108—109°/0.5 mm. [hydrogenated ($Pd-CaCO_3$ in $EtOH$) to α -phenylbutan- γ -ol (I), identified as the phenylurethane, m.p. 112—114°], and a bimol. compound, $C_{20}H_{20}OBr_2$, b.p. 200—210°/5 mm. Passage of a small excess of Cl_2 through a solution of $CHPh\cdot C\cdot CHMe$ in CCl_4 affords a product, $C_{10}H_{10}Cl_2$, b.p. 130°/13 mm., converted by aq. KOH into a mixture of $C_{10}H_9Cl$, $C_{10}H_{11}OCl$, and $C_{10}H_{10}Cl_2$ from one portion of which (I) is obtained by hydrogenation, and by $KOH-H_2O-EtOH$ into a mixture which is hydrogenated and then oxidised to a small amount of $Ph\cdot [CH_2]_2\cdot COMe$. The product obtained from HCl and $OH\cdot CHPh\cdot CCl\cdot CHMe$ is a mixture of $CHPhCl\cdot CCl\cdot CHMe$ and $CHPh\cdot CCl\cdot CHMeCl$. When treated with KOH in boiling aq. $COMe_2$ it gives a material, b.p. 100—105°/0.7 mm., which is hydrogenated ($Pd-CaCO_3$ in $KOH-EtOH$) to a substance, $C_{10}H_{14}O$, b.p. 105—110°/10

mm. (phenylurethane, m.p. 114—115°). Oxidation by CrO_3 gives a mixture of CH_2EtBz and $\text{Ph}[\text{CH}_2]_2\text{COMe}$, recognised as their semicarbazones. $\text{CHPh}:\text{CCl}:\text{CHMeCl}$ is nearly the sole product of the action of SOCl_2 on $\text{OH}:\text{CHPh}:\text{CCl}:\text{CHMe}$. Gradual addition of Br in CS_2 to α -cyclohexyl- $\Delta^{\beta\gamma}$ -pentadiene (II) causes slight evolution of HBr and yields a dibromide, $\text{C}_{11}\text{H}_{18}\text{Br}_2$, b.p. 110—115°/1 mm., which is practically unchanged by boiling dil. aq. alkali. The dichloro- α -cyclohexylpentene derived from γ -chloro- α -cyclohexyl- Δ^{γ} -penten- β -ol is likewise inert under the same conditions. Addition of Br (\equiv 2 atoms) to $\text{CHMe}:\text{C}:\text{CHMe}$ gives a dibromide, b.p. 87—90°/25 mm. Br is rapidly absorbed by $\text{CHPh}:\text{C}:\text{CHMe}$ in well-cooled MeOH, yielding much HBr and a mixture of $\text{C}_{11}\text{H}_{13}\text{OBr}:\text{OMe}$ and $\text{C}_{10}\text{H}_{10}\text{Br}_2$. Under similar conditions (II) gives a mixture of $\text{C}_{12}\text{H}_{21}\text{OBr}:\text{OMe}$ and $\text{C}_{11}\text{H}_{18}\text{Br}_2$, and $\text{CHMe}:\text{C}:\text{CHMe}$ affords $\text{C}_6\text{H}_{11}\text{OBr}$ and $\text{C}_5\text{H}_8\text{Br}_2$. Three compounds containing the cumulated system of double linkings react in indifferent solvents with Br (\equiv 2 atoms) to form Br_2 -additive compounds. In alcoholic solution Br and these substances furnish bromoalkoxy-additive products with liberation of free HBr. Pyrethron (III) in MeOH gives a partly methoxylated product. The reactions of (III) with Br in both classes of solvent are strictly analogous with those of the allenenes. Its behaviour therefore, is not incompatible with the presence of the cumulated system of double linkings in its side-chain which from the facts now available seems the most likely arrangement.

H. W.

Synthesis of condensed ring compounds. III. Hexahydronaphthalene derivative from a dieneine. L. W. BUTZ, A. M. GADDIS, E. W. J. BUTZ, and R. E. DAVIS (J. Org. Chem., 1940, 5, 379—387).— $\text{CH}_2:\text{CMe}:\text{C}:\text{CMe}:\text{CH}_2$ and $(\text{CH}:\text{CO})_2\text{O}$ at 130° give probably 1:5-dimethyl-2:3:4:6:7:8-hexahydronaphthalene-xxxy- or -xxxx-3:4:7:8-tetra-carboxydianhydride, m.p. 262—263° (bath preheated to 220°). It slowly decolorises KMnO_4 in COMe_2 , and absorbs Br in AcOH and 1.5 mols. of H_2 ($\text{EtOH}:\text{Pd}$). With EtOH it slowly forms the corresponding Et_4 ester, m.p. 163—165° (corr.). With Pd-C at 325—355° it yields 1:5- $\text{C}_{10}\text{H}_6\text{Me}_2$, also obtained by heating the Ba_2 salt with Pd-C and $\text{Ba}(\text{OH})_2$ at 450—500°.

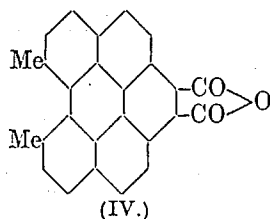
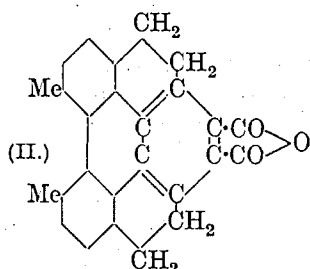
H. W.

Synthesis of methylchrysenes and related compounds. W. E. BACHMANN and W. S. STRUVE (J. Org. Chem., 1940, 5, 416—429).—2-Acetylphenanthrene is converted by $\text{Al}(\text{OPr}^t)_3$ in boiling Pr^tOH into 2-phenanthrylmethylcarbinol, m.p. 131—131.5°, transformed by PBr_3 in cold Et_2O into α -2-phenanthryl-ethyl bromide, m.p. 86—88°, which is converted by $\text{CHNa}(\text{CO}_2\text{Et})_2$ in EtOH followed by hydrolysis and decarboxylation into β -2-phenanthrylbutyric acid, m.p. 137.5—138.5° (lit. 125—127°). Successive treatments of the acid with SOCl_2 in dry Et_2O containing a little $\text{C}_5\text{H}_5\text{N}$, CH_2N_2 in Et_2O , Ag_2O in MeOH, and boiling 45% KOH lead to γ -2-phenanthrylvaleric acid, m.p. 136.5—138.5°, which is cyclised by the successive actions of SOCl_2 in $\text{Et}_2\text{O}:\text{C}_5\text{H}_5\text{N}$ and SnCl_4 in CS_2 to 6-keto-3-methyl-3:4:5:6-tetrahydrochrysene (I), prisms, m.p. 98.5—99.5°, or leaflets, m.p. 75—77°. This is reduced (Clemmensen) to 3-methyl-3:4:5:6-

tetrahydrochrysene (I), m.p. 120.5—121° (picrate, m.p. 124—124.5°), and converted by the successive actions of MgMeI and Pd-C at 300—320° into 3:6-dimethylchrysene, m.p. 141.5—142.5° (picrate, m.p. 140.5—141°). γ -1-Phenanthrylbutyric acid, m.p. 154—155.5°, is obtained by lengthening the chain of β -1-phenanthrylpropionic acid or by dehydrogenating (Pd-C at 250—260°) and subsequently hydrolysing $\text{Me } \gamma$ -1:1:2:3:4-tetrahydrophenanthryl butyrate. Its chloride is cyclised by SnCl_4 in C_6H_6 at room temp. to 3-keto-3:4:5:6-tetrahydrochrysene (II), m.p. 228—229°, which with MgMeI followed by Pd-C affords 3-methylchrysene, m.p. 249.5—250° [also obtained by dehydrogenation (Pd-C at 300—320°) of (I)], and with EtI similarly yields 3-ethylchrysene, m.p. 183—184°. Addition of (II) and $\text{Me}_2\text{C}_2\text{O}_4$ to NaOMe in MeOH gives $\text{Me } 3$ -keto-3:4:5:6-tetrahydrochrysene-4-glyoxylate, pale yellow leaflets, m.p. 169—170°, which change to dark yellow prisms, m.p. 176—177° (decomp.), converted at 180—190° in presence of powdered glass into $\text{Me } 3$ -keto-3:4:5:6-tetrahydrochrysene-4-carboxylate, m.p. 156.5—157.5°, which gives a green colour with FeCl_3 . This is transformed by NaOMe and MeI in boiling $\text{MeOH}:\text{C}_6\text{H}_6$ into $\text{Me } 3$ -keto-4-methyl-3:4:5:6-tetrahydrochrysene-4-carboxylate, m.p. 154—155°, which does not give a colour with FeCl_3 in EtOH and is hydrolysed and decomposed by boiling conc. $\text{HCl}:\text{AcOH}$ to 3-keto-4-methyl-3:4:5:6-tetrahydrochrysene, m.p. 184—184.5°. Reduction (Clemmensen) of the ketone affords 4-methyl-3:4:5:6-tetrahydrochrysene, m.p. 145—146°. Reaction of $\text{CHNa}(\text{CO}_2\text{Et})_2$ with ω -bromo-2-acetylphenanthrene followed by hydrolysis and decarboxylation of the product yields β -2-phenanthryl- α -methylpropionic acid, m.p. 228—229°, reduced (Zn-Hg and conc. HCl in AcOH) to α -2-phenanthryl- α -methylbutyric acid, m.p. 124—124.5°. The corresponding chloride is cyclised by SnCl_4 in CS_2 to 6-keto-5-methyl-3:4:5:6-tetrahydrochrysene (III), m.p. 114—115.5°. 6-Keto-3:4:5:6-tetrahydrochrysene, $\text{Me}_2\text{C}_2\text{O}_4$, and NaOMe in C_6H_6 at room temp. afford $\text{Me } 6$ -keto-3:4:5:6-tetrahydrochrysene-5-glyoxylate, m.p. 116—117.5°, converted at 180° in presence of glass into $\text{Me } 6$ -keto-3:4:5:6-tetrahydrochrysene-5-carboxylate, m.p. 154—155°, which gives an emerald-green colour with FeCl_3 . This with NaOMe and MeI in C_6H_6 yields $\text{Me } 6$ -keto-5-methyl-3:4:5:6-tetrahydrochrysene-5-carboxylate, m.p. 115.5—117°, which does not give a colour with FeCl_3 and is converted by conc. HCl and AcOH into (III). This ketone is reduced (Clemmensen) to 5-methyl-3:4:5:6-tetrahydrochrysene, m.p. 130—131°, dehydrogenated (Pd-C at 300—320°) to 5-methylchrysene, m.p. 170—170.5° (picrate, m.p. 164—164.5°). β -1:2:3:4-Tetrahydro-7-phenanthrylpropionic acid, m.p. 158—159°, is reduced (Clemmensen) to γ -1:2:3:4-tetrahydro-7-phenanthrylbutyric acid, m.p. 95.5—97°, the structure of which is proved by its dehydrogenation to γ -2-phenanthrylbutyric acid, m.p. 133.5—134.5°. The corresponding chloride is cyclised by SnCl_4 in C_6H_6 to 6-keto-3:4:5:6:9:10:11:12-octahydrochrysene, leaflets, m.p. 93.5—95°, or needles, m.p. 89.5—91° and, after resolidification, m.p. 93.5—95°, which is transformed by MgMeI followed by dehydration and dehydrogenation into 6-methylchrysene, m.p. 149—149.5°.

H. W.

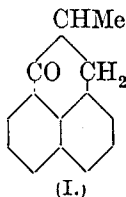
Synthesis of coronene. M. S. NEWMAN (J. Amer. Chem. Soc., 1940, 62, 1683—1687).—1-Keto-7-methyl-1:2:3:4-tetrahydronaphthalene (modified prep.), freshly scratched Al foil, and a little HgCl_2 in boiling abs. $\text{EtOH}-\text{C}_6\text{H}_6$ give 75–86% of *di*-(7-methyl-3:4-dihydronaphthyl), m.p. 110.0–111.6°, which with $(\text{CH}_3\text{CO})_2\text{O}$ in boiling xylene gives 1:2:7:8:9:10:8a:10a-octahydrodi-(4'-methylbenzo-1':2')-3:4:6:5-phenanthrene-9:10-dicarboxylic anhydride [9:12-dimethyl-1:2:2a:3:4:4a:5:6-octahydrodibenzo(c, g)phenanthrene-3:4-dicarboxylic anhydride] (73%), of which isomerides, (A) polymorphic forms, m.p. 218–220°, 231–232°, and 241–244° (decomp.), and (B) m.p. 226.0–226.6°, are isolated. With Br in $\text{CHCl}_3-\text{AcOH}$, (A) gives a small yield of a substance, $\text{C}_{26}\text{H}_{19}\text{O}_3\text{Br}$, m.p. 217.4–219.4°. With $\text{Pb}(\text{OAc})_4$, (A) or (B) or mixtures thereof give 1:2:7:8-tetrahydrodi-(4'-methylbenzo-1':2')-3:4:6:5-phenanthrene-9:10-dicarboxylic anhydride (I) (73%), dimorphic, m.p. 227–229°, and a small amount of (?) 1:12-dimethyl-4:5:8:9-tetrahydro-6:7-benzoperylene-5':6'-dicarboxylic anhydride (II), m.p. 274–275°. With Pd-C at 320–350°, (I) gives H_2 , *di*-(4'-methylbenzo-



1':2')-3:4:6:5-phenanthrene-9-carboxylic acid (III) (71%), m.p. 287–289°, and a little of the corresponding 9:10-dicarboxylic anhydride (IV), m.p. 298–301° (decomp.). Attempts at simple decarboxylation of (III) failed, but with KOH at, best, 320° (III) or (IV) or mixtures thereof give 5.5% of coronene, m.p. 438–440°, sublimes from 400° or at 380°/0.5 mm. [red picrate, decomp. from 250°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. from 280° (decomp.)]. The Me of (III) and (IV) must be spatially distorted. M.p. are corr.

R. S. C.

9-Methyl-3:4-benzpyrene. L. F. FIESER and F. C. NOVELLO (J. Amer. Soc., 1940, 62, 1855–1859).— $\alpha\text{-C}_{10}\text{H}_7\text{-CH}_2\text{Cl}$, b.p. 120–125°/1 mm., $\text{CHMe}(\text{CO}_2\text{Et})_2$ (prep. in 88% yield described), and $\text{NaOMe}-\text{MeOH}$ give $\alpha\text{-C}_{10}\text{H}_7\text{-CH}_2\text{CMe}(\text{CO}_2\text{Et})_2$ (70.5%), b.p. 175–176°/1 mm., converted by $\text{KOH}-\text{H}_2\text{O}-\text{EtOH}$ into β -1-naphthylisobutyric acid (73%), m.p. 91.8–92.6°, which in HF gives 8-methylperinaphthan-7-one (I), (96%), b.p. 135–136°/0.5 mm. [thermolabile oxime, m.p. 147.2–148.2°; $\text{K}_2\text{Cr}_2\text{O}_7-\text{AcOH}$ gives 1:8- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$]. Mossy Zn-Hg-conc. $\text{HCl}-\text{MeOH}-\text{C}_6\text{H}_6$ reduces (I) to 8-methylperinaphthane (70%), b.p. 135°/1.5 mm. [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 149–150° (decomp.)], unstable to air and light, which with $\text{AlCl}_3-\text{BzCl}$ in CS_2 at 0° gives 3-benzoyl-8-methylperinaphthane (78%), b.p. 215–220°/2 mm. [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 107.4–108.4°].



With NaCl and AlCl_3 at 130°, later 130–150°, this gives a tar, which, when distilled with Zn dust, gives 1% of 9-methyl-3:4-benzpyrene, m.p. 147.2–148° [isolated by way of the $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 218.5–219.5°, and chromatography], with some 3:4-benzpyrene and a mixture of hydrides. Prep. of 4'-keto-1':2':3':4'-tetrahydro-3:4-benzpyrene in 85–95% yield from γ -1-pyrenylbutyric acid by $\text{PCl}_5-\text{C}_6\text{H}_6$, followed by SnCl_4 , is described. Ozonisation of 3:4-benzpyrene gives indefinite products. O_3 and pyrene in EtOAc give an ozonide, decomposed by $\text{H}_2-\text{Pd}-\text{CaCO}_3$ to 4-aldehydophenanthrene-5-carboxylic acid (27%), m.p. 279–280° (the dialdehyde could not be obtained), which with H_2-Cu chromite in abs. EtOH at 130°/1400 lb. gives *Et* 4-hydroxymethylphenanthrene-5-carboxylate, m.p. 177.5–178°; after more prolonged ozonisation, hydrogenation gives diphenyl-2:6:2':6'-tetra-aldehyde, m.p. 162–162.8° [(? tetra)phenylhydrazone, m.p. 193–197°; tetraoxime monoacetate (prep. by $\text{NH}_2\text{OH}, \text{HCl}-\text{NaOAc}$ in H_2O), m.p. 273° (decomp.)]; more prolonged hydrogenation gives 2:6:2':6'-tetra(hydroxymethyl)diphenyl, m.p. 171.2–172°. Pyrene is freed from S by Na at 210–223°, then has m.p. 147–148°, and is suitable for hydrogenation (Cu chromite; gives the *as*- H_4 -derivative, m.p. 103–105°, and a substance, m.p. 87–93.5°); after further purification by $(\text{CH}_3\text{CO})_2\text{O}$ it has m.p. 150.9–151.1°. M.p. are corr.

R. S. C.

Steric inhibition of resonance.—See A., 1940, I, 353.

Sulphanilamide compounds. IV. N^4 -Aryl- and N^4 -arylidene- N^1 -substituted sulphanilamides. H. G. KOLLOFF and J. H. HUNTER (J. Amer. Chem. Soc., 1940, 62, 1647–1649; cf. A., 1940, II, 330).—Hydrogenation (Raney Ni; dioxan; 3 atm.) of the arylidene derivatives gives N^4 -benzyl-, m.p. 174.5–175.8°, and N^4 -*p*-methoxybenzyl-, m.p. 177–178°, N^1 -phenyl- N^4 -benzyl-, m.p. 177.5–178.1°, N^1 -phenyl- N^4 -*p*-methoxybenzyl-, m.p. 162–162.4°, N^1 -pyridyl- N^4 -*p*-methoxybenzyl-, m.p. 216.5–217.5°, N^4 -acetyl- N^1 -*p*-benzylaminophenyl- (I), m.p. 182–182.5°, N^4 -acetyl- N^1 -*p*-*p'*-methoxybenzylaminophenyl-, m.p. 208–208.5°, N^1 -*p*-benzylaminophenyl- [prep. from (I) by boiling 5% NaOH], m.p. 175–175.5°, N^1 -*p*-*p'*-methoxybenzylaminophenyl-, m.p. 157–157.5°, and $\text{N}-p-p'$ -methoxybenzylaminophenyl- N^4 -*p*-methoxybenzyl-, m.p. 184–185°, -sulphanilamide. N^1 -*o*-Carboxyphenyl- N^4 -benzylidene-, m.p. 226–226.5°, -*p*-anilylidene-, m.p. 233–233.5°, and -*p*-dimethylaminobenzylidene-, m.p. 247–248°, N^4 -*p*-nitrobenzylidene-, m.p. 187.5–188°, N^1 -phenyl-, m.p. 196–197°, and N^1 -*p*-nitrophenyl- N^4 -*p*-nitrobenzylidene-, m.p. 201.5–202°, N^1 -2-pyridyl- N^4 -*o*-, m.p. 193–194°, and -*p*-nitrobenzylidene-, m.p. 245–246.2°, and N^1 -2-pyridyl- N^4 -*m*-hydroxybenzylidene-sulphanilamide, m.p. 242–243.5°, are prepared as previously described (A., 1940, II, 76).

R. S. C.

Reduction of xyleneazo- β -naphthol. W. SEAMAN, A. R. NORTON, and J. HUGONET (Ind. Eng. Chem. [Anal.], 1940, 12, 464–465).—Xyleneazo- β -naphthol (commercial product) is reduced with Zn dust and conc. HCl in dioxan and the recovered mixed xylidines (90–95% yield) are analysed (method: B., 1940, 657) for *m*-xylidines. J. D. R.

Phenolic substances of white hellebore (*Veratrum grandiflorum*, Loes. Fil.). M. TAKAOKA (J. Fac. Sci. Hokkaido, 1940, [iii], 3, 1—16).—The phenolic substances isolated from the roots by the method of Saito *et al.* (A., 1936, 870) contain *resveratrole* (I), $C_{14}H_{12}O_3$ (0.07%), m.p. 261° (*triacetate*, m.p. 114—116°), and *hydroxyresveratrole* (II), $C_{14}H_{12}O_4 \cdot 2H_2O$ (II) (0.03%), m.p. 199.5°; a *phytosterolglucoside* (III) (0.02% of the dried roots) is also isolated. (I) gives no reactions for CO; Zn dust distillation yields PhOH. Oxidation (CrO_3) of its Me_3 ether, m.p. 56—57°, which is unaffected by Pd-black in C_6H_6 , gives, in the cold, 3:5:1-(OMe) $_2$ C $_6$ H $_3$ ·CHO (IV), and in the hot, p -OMe-C $_6$ H $_4$ ·CO $_2$ H. The absorption spectra of stilbene, 4-hydroxy- and -acetoxy-stilbene closely resemble those of the triacetate and Me_3 ether of (I), which is therefore 3:5:4'-*trihydroxystilbene*. 3:5-Dimethoxyphenyl 4-methoxycinnamate, m.p. 81—83°, when heated at 305—315° in N_2 or dry distilled with Cu yields 4:4'-dimethoxystilbene, whilst (IV) heated with p -OMe-C $_6$ H $_4$ ·CH $_2$ ·CO $_2$ H gives a substance, $C_{18}H_{16}O_5$ (?), m.p. 174°, possibly 6:8-dimethoxy-3-*p*-anisylcoumarin. 3:5-Dimethoxyphenylacetic acid, m.p. 104—105° [prep. by methylation of the (OH) $_2$ -acid] [as Na salt (V)], with p -OMe-C $_6$ H $_4$ ·CHO in Ac_2O at 165—170° yields 3:5:4'-*trimethoxystilbene- α -carboxylic acid*, m.p. 182°, which with Cu in quinoline gives an oily product reduced (Na + EtOH) and then brominated (in CS_2) to a *dibromo*-3:5:4'-*trimethoxy- $\alpha\beta$ -diphenylethane*, m.p. 133—134°, identical with that similarly obtained from the Me_3 ether of (I). Distillation of (II) with Zn dust yields m -C $_6$ H $_4$ (OH) $_2$. Oxidation (CrO_3) of its *tetra-acetate*, m.p. 141—142°, yields 3:5:1-(OAc) $_2$ C $_6$ H $_3$ ·CO $_2$ H; the *tetrabenzoate*, m.p. 193.5°, yields α -, m.p. 224—226°, and β -, m.p. 152°, *-dibenzoyltresorcylic acid*. These results and the absorption spectrum indicate that (II) is 3:5:2':4'-*tetrahydroxystilbene*. 2:4:1-(OMe) $_2$ C $_6$ H $_3$ ·CHO, (V), and Ac_2O yield 3:5:2':4'-*tetramethoxystilbene- α -carboxylic acid*, m.p. 181.5°, decarboxylation, reduction, and bromination of which yields *tribromo*-3:5:2':4'-*tetramethoxy- $\alpha\beta$ -diphenylethane*, m.p. 185—186°, also similarly prepared from the oily Me_3 ether of (II). (III) is identical with the *phytosterolin* obtained by Nakamura *et al.* (A., 1931, 606) from wheat-germ oil. 2:4:1-(OH) $_2$ C $_6$ H $_3$ ·CHO, 3:5:1-(OH) $_2$ C $_6$ H $_3$ ·CH $_2$ ·CO $_2$ Na, and Ac_2O at 165—175° yield a neutral compound, $C_{21}H_{16}O_8$, m.p. 186—187°, probably the lactone of 2'-hydroxy-3:5:4'-*triacetoxystilbene- α -carboxylic acid*. A. Li.

Difficultly decomposable xanthates. P. V. LAAKSO (Suomen Kem., 1940, 13, B, 8—12).—2:2:6:6-Tetramethylcyclohexanol forms "labile" xanthates, e.g., OR·CS $_2$ Me (type *a*) which partially (20—25%) isomerise and partially decompose when heated to 230° giving RS·CO·SMe ("stable"; type *b*). The following have been prepared: *Me*, (a) m.p. 60—60.5°, b.p. 159—160°/17 mm., (b) m.p. 56—56.5°, b.p. 161—162°/14 mm., *Et*, (a) b.p. 163—164°/14 mm. and (b) 175—177°/18 mm., *Pr*^a, (a) b.p. 154—155°/7 mm., and (b) 160—163°/7 mm., and *Pr*^b, (a) b.p. 160—168°/15 mm. and (b) 179—181°/18 mm. With KOH-EtOH (b) give 1-thiol-2:2:6:6-tetramethyl-

cyclohexane (I), m.p. 35—36°, b.p. 81—82°/7 mm., which undergoes partial atm. oxidation to an oxide, (C $_{10}$ H $_{18}$ S) $_2$ O, m.p. 107—107.5°. With I, (I) slowly gives the *disulphide*, m.p. 59—59.5°. When heated with aq. glycerol (*a*) are mainly decomposed, but partly isomerised to (*b*), which decompose much more slowly than (*a*). Ultra-violet irradiation of (*b*) in EtOH for 10 days causes loss of CO and formation of 2:2:6:6-tetramethylcyclohexyl Me disulphide (II), which then loses MeSH (giving 1-thion-2:2:6:6-tetramethylcyclohexane) or CH $_2$ S [giving (I)]; (*a*) are similarly unchanged. With NH $_3$ -EtOH (*b*) give (I) whilst (*a*) afford an *amine*, m.p. 194.5—195.5°. Fenchyl, CHBu $_2$, and 1-methylcyclohexyl Me xanthates similarly give *isomerides* (type *b*), b.p. 171—173°/20 mm., [α] $_D^{25}$ -24.64°, b.p. 148—150°/20 mm. (m.p. 8—9°), and —, respectively, in yields of 5—20, 70, and 2.5%, respectively. Na fenchyl xanthate does not isomerise on heating. Fenchyl Me disulphide, b.p. 146—148°/20 mm., [α] $_D^{25}$ -97.08°, thiofenchone, b.p. 101—103°/20 mm., γ -thiol- $\beta\beta\delta\delta$ -tetramethylpentane, b.p. 82—85°/20 mm., and the *oxide*, (CHBu $_2$) $_2$ S $_2$ O, m.p. 128—129°, are prepared. The Na salt of (I) is prepared from (II) and Na in Et $_2$ O; (I) is insol. in aq. alkali hydroxides. M. H. M. A.

Reaction of the esters of phenylglycine and phenylalanine on Raney catalyst. G. OVAKIMIAN, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1940, 135, 91—98; cf. A., 1940, II, 170, 269).—*d*-NH $_2$ ·CHPh·CO $_2$ Et, [α] $_D^{25}$ -113° (I) or -52.4° (II) (homogeneous), is not satisfactorily reduced by H $_2$ and Cu chromite, but with Raney Ni and H $_2$ at 150 atm. in MeOH yields, at 40° for 9 hr., β -amino- β -phenyl-, b.p. 91—98°/0.1 mm., [α] $_D^{25}$ -15.0° [from (I)] (*picrate*, m.p. 208—210°) or -7.8° [from (II)] in MeOH, and at 40° for 44 hr., β -amino- β -cyclohexylethyl alcohol (III), b.p. 95—105° (bath temp.)/0.1 mm., [α] $_D^{25}$ -4.8° in MeOH [from (I)]. Similar reduction of *dl*-NH $_2$ ·CHPh·CO $_2$ Et yields, at 40° for 18 hr., *dl*-(III), b.p. 130—135° (bath temp.)/0.5 mm., at 135° for 9 hr., β -dimethylamino- β -cyclohexylethyl alcohol (IV), b.p. 140°/20 mm. (*picrate*, m.p. 92—93°), and at 185° for 9 hr., (IV), α -dimethylamino- α -cyclohexylethane, b.p. 80° (*picrate*, m.p. 131°), and 2:5-dicyclohexyl-NN'-dimethylpiperazine, b.p. 150°/5 mm. (*dipicrate*, m.p. 230—235°). CH $_2$ Ph·CH(NH $_2$)·CO $_2$ Me is similarly reduced at 185° to β -dimethylamino- α -cyclohexylpropane, b.p. 90°/10 mm. (*picrate*, m.p. 145—146°), and 2:5-dihexahydrobenzyl-NN'-dimethylpiperazine, b.p. 150°/5 mm. (*dipicrate*, m.p. 144—146°). NH $_2$ ·CHPh·CO $_2$ Me and CH $_2$ Ph·CH(NH $_2$)·CO $_2$ Me when heated at 160—170° for 9 hr. in MeOH yield 3:6-diketo-2:5-diphenyl-, m.p. 270°, and *-dibenzyl-piperazine*, m.p. 295—296°, respectively. A. Li.

Intermediates in the preparation of sympathol [β -methylamino- α -*p*-hydroxyphenylethyl alcohol]. H. M. PRIESTLEY and E. MONESS (J. Org. Chem., 1940, 5, 355—361).—Little reaction is observed between PhOBz and CH $_2$ Cl·COCl with POCl $_3$ in boiling C $_6$ H $_6$ or with AlCl $_3$ in CS $_2$; with AlCl $_3$ alone at 120° *p*-chloroacetoxybenzophenone, m.p. 123° (hydrolysed by fuming HCl at room temp. to *p*-C $_6$ H $_4$ Bz·OH), is obtained. α -Chloro-*p*-benzoyloxyacetophenone has m.p. 115°. *p*-C $_6$ H $_4$ Ac·OH, CH $_2$ PhCl, and boiling

EtOH-NaOEt afford *p*-benzyloxyacetophenone (I), m.p. 93° (the *o*-isomeride has m.p. 40°), which with Br in CHCl₃ gives α -mono- (II), m.p. 91°, or $\alpha\alpha$ -dibromo-*p*-benzyloxyacetophenone, m.p. 84°. (II) and CH₂Ph-NHMe yield *p*- α -benzylmethylaminobenzoyloxyacetophenone, a gum, catalytically reduced to symphathol. *p*-C₆H₄Ac·OH and Br in aq. AcOH give 3 : 5-dibromo-4-hydroxyacetophenone, m.p. 181° (phenylhydrazine, m.p. 147°), converted by Me₂SO₄ and NaOH into the Me ether, which is oxidised by HNO₃ to 4 : 3 : 5 : 1-OMe·C₆H₂Br₂·CO₂H. 3 : 5-Dibromo-4-benzyloxyacetophenone, m.p. 79°, its α -bromo-, m.p. 119°, and $\alpha\alpha$ -dibromo-, m.p. 104°, derivatives are described. 3 : 5-Dibromo-4-hydroxy- α -bromo-, and - $\alpha\alpha$ -dibromo-acetophenone have m.p. 128° and 105°, respectively. α -Oximino-*p*-benzyloxyacetophenone, m.p. 149°, best obtained from (I) and an excess of NaOEt and OBU·NO, is reduced (Pd-C in EtOH containing HCl) to α -amino-*p*-benzyloxyacetophenone (hydrochloride, m.p. 226°). (I), OBU·NO, and HCl in C₆H₆ give a little *p*-CO₂H·C₆H₄·O·CH₂Ph, m.p. 187°. 3 : 4-Dibenzyloxybenzoic acid, m.p. 182°, is obtained by the action of NaOEt and OBU·NO on 3 : 4-dibenzyloxy-propiophenone or -acetophenone.

II. W.

Unsaturated steroids. VII. Action of perbenzoic acid on Δ^2 -cholestadiene. W. BERGMANN and E. L. SKAU (J. Org. Chem., 1940, 5, 439—442; cf. A., 1939, II, 217).— Δ^2 -cholestadiene (I) and BzO₂H (1 mol.) in CHCl₃ at 0° give 4 : 5-dihydroxy- Δ^2 -cholestene (II), m.p. 136—136.5°, [α]_D²⁵ +132° in C₅H₅N, which is stable towards KOH-EtOH and converted by boiling Ac₂O into the 4-monoacetate, m.p. 159—160°, [α]_D²⁵ +16° in COMe₂. (II) is hydrogenated (PtO₂ in EtOAc) to 4 : 5-dihydroxycholestane, m.p. 171—172°, [α]_D²⁵ +35.5° in COMe₂ (4-monoacetate, m.p. 174—175°), which reacts with 1 mol. of Pb(OAc)₄ indicating the presence of 2 OH in adjacent positions. With 2 mols. of BzO₂H, (I) gives a substance, C₂₇H₄₄O₂Cl, m.p. 112—113° [α]_D²⁵ +72° in COMe₂, which loses HCl when boiled with 0.05N-MeOH-KOH giving a (?) dioxidocholestane, C₂₇H₄₄O₂, m.p. 120—121° and, after resolidification, m.p. 134.5—135°, [α]_D²⁵ +76° in Et₂O. It is unchanged when distilled in a vac. or treated with BzCl in C₅H₅N or NH₂OH in MeOH. When refluxed with Ac₂O or treated with glacial AcOH containing a trace of H₂SO₄ at room temp. decomp. occurs. H. W.

Preparation and oxidation of substituted cinnamic acids. V. S. WEBSTER (Amer. J. Pharm., 1940, 112, 291—296).—Substituted vanillins by the Perkin synthesis yield 2-, m.p. 202—203°, 5-, m.p. 243—244°, and 6-bromo-, m.p. 229—230°, 5 : 6-dibromo-, m.p. 278° (decomp.), 2-nitro-, m.p. 210° (decomp.), and 5-chloro-, m.p. 235—236°, 4-hydroxy-3-methoxycinnamic acid. Oxidation (cold aq. Na₂CO₃-KMnO₄) of the acetates, m.p. 202—203°, 212—213°, 211—212°, 212—213°, 166—167°, and 201°, respectively, of these yields 27—71% of the original vanillins but none of the corresponding acids. A. LI.

Carbobenzyloxyglycyl-L-phenylalanine, m.p. 125—126°, and L-glutamic acid, m.p. 160—162°, and α -hippuryl-L-llysine, m.p. 236—238°.—See A., 1940, III, 766.

Conversion of di-iodotyrosine into thyroxine. P. BLOCK, jun. (J. Biol. Chem., 1940, 135, 51—52).—Synthetic *dl*-di-iodotyrosine with aq. NaOH at 37° and *p*_H 8.8 for 14 days gives ~0.1% of thyroxine. The results of von Mutzenbecher *et al.* (A., 1940, III, 406) with natural material are thus confirmed.

A. LI.

Purification of phthalic anhydride.—See B., 1940, 657.

Curtius degradation with diphenic acid hydrazides. R. LABRIOLA (J. Org. Chem., 1940, 5, 329—333).—Diphenidihydrazide (I), m.p. 210—211°, from Me₂ diphenate and N₂H₄·H₂O at 150—160°, is converted by NaNO₂ and N-HCl into the unstable diazide, which in Et₂O·C₆H₆ affords *oo'*-diphenylenecarbamide (II), m.p. 308°, and 2 : 2'-diaminodiphenyl (III), m.p. 80—81°. In Et₂O-EtOH and Et₂O-MeOH it gives *oo'*-diphenylenedi-(ethylurethane), m.p. 131°, and -(methylurethane), m.p. 145°, respectively, hydrolysed by 5% NaOH-EtOH to (II) and (III). N-HCl, (I), and the requisite amount of NaNO₂ produce the very unstable diphenhydrazideazide, transformed by neutral EtOH into phenanthridone (IV) and by EtOH-HCl into (V) (below). Diphenmonohydrazide affords the unstable azide, which with Et₂O-EtOH gives (IV) and with a saturated solution of HCl in the requisite alcohol affords Me, m.p. 127°, Et (V), m.p. 143—144°, Pr^a, m.p. 76°, Pr^b, m.p. 123°, allyl, m.p. 93—94°, cyclohexyl, m.p. 151°, and CH₂Ph, m.p. 134°, phenanthridone-10-carboxylate. (V) is obtained from (IV), KOH, and ClCO₂Et at 120°. H. W.

1 : 4-Di(carboxymethoxy)-2-methylnaphthalene, m.p. 217—218° [from the naphthaquinol and CH₂Cl·CO₂H].—See A., 1940, III, 706.

Acids of the ætiocholane series.—See B., 1940, 701.

Derivatives of the dimethylpolyhydrocyclopentanophenanthrene series.—See B., 1940, 701.

Conversion of testosterone into ætioallocholan-3(β)-ol-17-one. R. I. DORFMAN and W. R. FISH (J. Biol. Chem., 1940, 135, 349—350; cf. A., 1939, III, 1057; 1940, III, 131).—Ætioallocholan-3(β)-ol-17-one has been isolated (by chromatographic adsorption on Al₂O₃ or pptn. with digitonin) from the urine of adult male guinea-pigs injected subcutaneously with testosterone propionate in olive oil. A. LI.

Walden inversion and the Hofmann rearrangement. S. ARCHER (J. Amer. Chem. Soc., 1940, 62, 1872).—Proof that the Hofmann reaction involves no inversion is provided by Noves' conversion of *cis*- β -camphoramidic acid by NaOBr into aminodihydrocampholytic acid (I), which with NaOAc-Ac₂O gives the lactam, hydrolysable to (I). R. S. C.

Saponins and sterols. XVI. Conversion of ursolic acid into uvaol. K. FUJII and S. OOSUMI (J. Pharm. Soc. Japan, 1940, 60, 71—72; cf. A., 1940, II, 221).—Uvaol (I) is ursolic acid in which CO₂H is replaced by CH₂OH, the following reactions being realised (no details): acetylursolic acid, m.p. 295—296° \rightarrow acetylursolyl chloride, m.p. 225° \rightarrow the Ph ester, m.p. 179—181°, thereof \rightarrow Ph ursolate \rightarrow (I), m.p. 232—233° (diacetate, m.p. 157—159°).

R. S. C.

Temisin. I. Y. ASAHINA, H. NAKAMURA, and T. UKITA (J. Pharm. Soc. Japan, 1940, **60**, 72—74).—Temisin, new formula, $C_{15}H_{22}O_3$, m.p. 228° , $[\alpha]_D^{20} +69.86^\circ$, with $Na_2Cr_2O_7$ -AcOH at 60 – 70° gives temisone (I), $C_{15}H_{20}O_3$, sinters at 125° , m.p. 131° , $[\alpha]_D^{20} -84.65^\circ$, and with H_2 -PtO₂ gives a H_2 -derivative (II), m.p. 231° , $[\alpha]_D^{20} +45.94^\circ$. $Na_2Cr_2O_7$ and (II) or H_2 -PtO₂ and (I) give tetrahydrotomisone, m.p. 109.5° (lit. 112°), $[\alpha]_D^{20} -63.75^\circ$. Na reduces (II) in *iso*- C_5H_{11} -OH to a triol, $C_{15}H_{30}O_3$, m.p. 148° , $[\alpha]_D^{23} +20.64^\circ$ [triacetate, b.p. 188° (bath)/ 0.07 mm., $[\alpha]_D^{23} +28.95^\circ$, $[M]_D^{25}$ 102.14]. These substances are thus monocyclic (cf. Nakamura *et al.*, A., 1933, 651; 1934, 1007). R. S. C.

Sapogenins of the Chinese drug yang-chiao-ou. J. H. CHU (Chinese J. Physiol., 1940, **15**, 309—314).—The chief active constituent of yang-chiao-ou [*Strophanthus divaricatus* (Lour), Hook and Arn] is an amorphous saponin (which gives dark red \rightarrow bluish-violet with H_2SO_4), hydrolysed by acids to glucose and three sapogenins, *strophanthilin A*, $C_{25}H_{36}O_4$, m.p. 205 – 206° , $[\alpha]_D^{25} +14.4^\circ$ in EtOH (diacetate, m.p. 200°), *B*, $C_{39}H_{64}O_4$, m.p. 289 – 291° (diacetate, m.p. 254 – 256°), and *C*, $C_{18}H_{24}O_4$, m.p. 305 – 307° . The Liebermann test gives with *A*, yellowish \rightarrow violet-blue, with *B*, pink, and with *C*, brownish \rightarrow violet-blue; the Liebermann-Burchard reaction gives with *A*, cherry-red \rightarrow green, and with *B*, pink. A. Li.

Coumarins. F. FUJIKAWA and S. INOUE (J. Pharm. Soc. Japan, 1940, **60**, 58—59).—1-Carboxy-oreinaldehyde 3-Me ether, Ac_2O , and $NaOAc$ at 180° give 7-acetoxy-, m.p. 126° , and thence (KOH) 7-hydroxy-5-methylcoumarin, m.p. 250° . Similarly are prepared 7-hydroxy-5:8-dimethyl-, m.p. 285° (*Ac* derivative, m.p. 142°), 6:7-dihydroxy-5:8-dimethyl-, m.p. 250° (*Ac*₂ derivative, m.p. 176°), and 7-hydroxy-5-n-propyl-, m.p. 105° (*Ac* derivative, m.p. 94°), -coumarin. R. S. C.

Synthesis of 5:6:4'- and 5:8:4'-trihydroxyflavone. Z. HORII (J. Pharm. Soc. Japan, 1940, **60**, 81—86).—2:5:6:1-(OH)₂C₆H₂(OMe)₂COMe (I) and OMe·C₆H₄·COCl in C_5H_5N at 100° give 2:5-di-*p*-anisoxyl-6-methoxyacetophenone, m.p. 183 – 185° (decomp. 197 – 198°), which with $NaNH_2$ in PhMe at 100° gives 2:6:5:1-OH·C₆H₂(OMe)(O·CO·C₆H₄·OMe-*p*)·CO·CH₂·CO·C₆H₄·OMe-*p* and thence by conc. H_2SO_4 at room temp. 6-hydroxy-5:4'-dimethoxyflavone (II), m.p. 214 – 215° (*Ac* derivative, m.p. 198°). With HI at 120 – 130° this gives a substance (III), converted by Ac_2O - C_5H_5N into an acetoxylflavone (IV), m.p. 219 – 220° . With 20% HCl or $AlCl_3$ -dioxan at 100° (II) yields 5:6-dihydroxy-4'-methoxyflavone, m.p. 211 – 212° (*Ac*₂ derivative, m.p. 216.5 – 217.5°). With Me_2SO_4 - K_2CO_3 in boiling COMe₂, (II) or (III) gives 5:6:4'-trimethoxyflavone (V), m.p. 165 – 165.5° . 2-Hydroxy-5:6-dimethoxyacetophenone [prep. from (I) by K_2CO_3 -COMe₂ at 40 – 50°], b.p. 163 – $165^\circ/24$ mm., gives similarly the 2-anisoxyl-, m.p. 104.5 – 105.5° , and 2-hydroxy- ω -*p*-anisoxyl-derivative, m.p. 70 – 71° , and (V). Boiling 20% HCl hydrolyses (V) to 5-hydroxy-6:4'-dimethoxyflavone, m.p. 179.5 – 180.5° (*Ac* derivative, m.p. 187 – 188°), but HI gives (III). 2:3:6:1-OH·C₆H₂(OMe)₂COMe gives similarly the 2-*p*-anisoxyl-, m.p. 131 – 132° , and 2-hydroxy- ω -*p*-

anisoxyl-derivative, m.p. 141 – 142° , and 5:8:4'-trimethoxyflavone, m.p. 164 – 165° , which with boiling HI (*d* 1.7) gives (III), m.p. $>300^\circ$ [and thence (IV)], or with $AlCl_3$ in PhNO₂ at 100° gives 5-hydroxy-8:4'-dimethoxyflavone, m.p. 132 – 134° , isolated as *Ac* derivative, m.p. 205.5 – 206.5° , and obtained therefrom by HCl-AcOH. R. S. C.

Reaction of 2-chloro-5-nitropyridine and thio-carbamide. A. R. SURREY and H. G. LINDWALL (J. Amer. Chem. Soc., 1940, **62**, 1697—1698).—Di-5-nitro-2-pyridyl sulphide (I) is obtained in 87% yield from 2-chloro-5-nitropyridine (II) and CS(NH₂)₂ in H_2O at 100° . In abs. EtOH a 1:1 additive compound (III), $C_6H_7O_2N_2S$, m.p. 187 – 190° (decomp.), is formed, but (I) is obtained if H_2O is present. With aq. Na_2CO_3 at 100° , (III) gives 5-nitro-2-thiopyridine (IV), but with H_2O at 100° slowly gives (I). (I) is better obtained from (IV) by (II) or, best, (IV) in H_2O . Formation of (I) in H_2O probably occurs by decomp. of (III) to give (IV), which then reacts with more (III). With CH_2Cl -CO₂H in H_2O at 100° , (III) or (IV) gives S-5-nitro-2-pyridylthiolacetic acid, m.p. 127 – 129° . R. S. C.

Sulphanilamide compounds. III. *N*⁴-Heteroacyl derivatives of *N*¹-substituted sulphanilamides. H. G. KOLLOFF and J. H. HUNTER (J. Amer. Chem. Soc., 1940, **62**, 1646—1647; cf. A., 1940, II, 76).—The following are prepared. *N*⁴-2-Furoyl-, m.p. 273.5° , -thiophen-2'-carboxyl-, m.p. 278 – 278.5° , -nicotinoyl-, m.p. 250° , and -*n*-hexoyl-, m.p. 205° , -sulphanilamide. *N*⁴-2-Furoyl-*N*¹-phenyl-, m.p. 243.5 – 244° , -*p*-nitrophenyl-, m.p. 259° , -*p*-aminophenyl-, m.p. 238 – 238.5° , and -2'-pyridyl-, m.p. 242° , -sulphanilamide. *N*⁴-Thiophen-2'-carboxyl-*N*¹-phenyl-, m.p. 228 – 230° , -*p*-nitrophenyl- (I) (from *p*-NH₂·C₆H₄·SO₂·NH·C₆H₄·NO₂-*p* by thiophen-2-carboxyl chloride in C_5H_5N at 100°), m.p. 261 – 262.5° , -*p*-aminophenyl- [from (I) by $FeSO_4$ -aq. NaOH-NH₃], m.p. 267.2° , and -2'-pyridyl-, m.p. 257 – 258° , -sulphanilamide. *N*⁴-Nicotinoyl-*N*¹-phenyl-, m.p. 222.8° , -*p*-nitrophenyl-, m.p. 267 – 269° , -*p*-aminophenyl-, m.p. 227° , and -2'-pyridyl-, m.p. 265 – 266° , -sulphanilamide. *N*⁴-*n*-Hexoyl-*N*¹-phenyl-, m.p. 190 – 190.5° , -*p*-nitrophenyl-, m.p. 225° , -*p*-aminophenyl-, m.p. 197.5 – 198° , and -2'-pyridyl-, m.p. 200 – 201° , -sulphanilamide. As a class these products are inferior to sulphanilamide against strepto- and pneumo-cocci. R. S. C.

Pyridine derivatives.—See B., 1940, 594.

Synthesis of 3-indolylacetic acid. J. TANAKA (J. Pharm. Soc. Japan, 1940, **60**, 75—76).—CN·[CH₂]₂·CH(OEt)₂ (I) and H_2SO_4 -CO₂ at 40 – 50° give CN·[CH₂]₂·CHO, b.p. 85 – $87^\circ/6$ mm. (semicarbazone, m.p. 163° ; *p*-nitrophenylhydrazone, m.p. 134°), the phenylhydrazone, m.p. 49 – 50° , of which with $ZnCl_2$ at 150° gives 3-indolylacetic acid, m.p. 165 – 166° , also obtained from (I) by $NHPh$ -NH₂ and $ZnCl_2$ -CaCl₂ at, first, 110 – 115° and later 150° . R. S. C.

Derivatives of 4-hydroxyquinoline. II. R. GILLIS, F. LIONS, and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1940, **73**, 258—262; cf. A., 1939, II, 181).—Interaction of $NHAr$ ·CMe·CH·CO₂Et, R₁, and $NaOEt$ -EtOH and subsequent heating at 260°

gives 50—90% of 4-hydroxy-2:3-dimethylquinoline, m.p. 217°, 4-hydroxy-2-methyl-3-ethyl-, m.p. 275°, -3-n-propyl-, m.p. 263°, -3-allyl-, m.p. 273°, and -3-butyl-, m.p. 237°, -isoquinoline, 4-hydroxy-2:3-dimethyl-5:6-benzoquinoline, 4-hydroxy-2-methyl-3-ethyl-, -3-n- and -3-iso-propyl-, -3-butyl-, -3-benzyl-, and -3- β -phenylethyl-5:6-benzoquinoline, m.p. >300°. β -C₁₀H₇·NH·CMe·CH·CO₂Et and (CH₂Br)₂ give $\alpha\beta$ -bis-4-hydroxy-2-methyl-5:6-benzo-5(?3)-quinolyethane, m.p. >300°. R. S. C.

Synthesis of octahydropyrrocolines. F. LIONS and A. M. WILLISON (J. Proc. Roy. Soc. New South Wales, 1940, 73, 240—252).—CO(CH₂·CO₂Et)₂, NH₂[CH₂]₃·CH(OEt)₂, and CH₂O give 88% of Et₂ 7-keto-octahydropyrrocoline-6:8-dicarboxylate, an oil, decomp. when distilled, and thence by partial acid hydrolysis Et 7-keto-octahydropyrrocoline-6- or -8-carboxylate (12%), m.p. 60° (picrate, m.p. 137°), or by prolonged hydrolysis in presence of Zn 7-keto-octahydropyrrocoline (24%), b.p. 104—105°/18 mm. (picrate, m.p. 198—200°). Clemmensen reduction then gives octahydropyrrocoline, b.p. 60°/15 mm. [picrate, m.p. 215° (decomp.); platinichloride, m.p. 203° (decomp.)]. Use of RCHO in place of CH₂O leads to Et₂ 7-keto-5-methyl-, m.p. 102° (picrate, m.p. 150°), and -5-isopropyl- (picrate, m.p. 135°) octahydropyrrocoline-6:8-dicarboxylate, 7-keto-6-methyloctahydropyrrocoline, b.p. 119°/20 mm. [picrates, m.p. 194° (decomp.) and decomp. ~188°], 5-methyl-, b.p. 79°/15 mm. [picrates, m.p. 235° (decomp.) and 196° (decomp.); platinichloride, softens at 170°, decomp. 220°], 5-isopropyl-, b.p. 99—101°/23 mm. [picrolonate, m.p. 197° (decomp.)], and 5-phenyl-octahydropyrrocoline (16%), b.p. 155°/20 mm. (picrates, m.p. 174° and 193°), and oily intermediates. The final products are unstable to air and light. Piperonal did not condense. R. S. C.

4:5-Ethyleneisoquinoline derivatives. A. FLACK and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1940, 73, 253—257).—1-Hydrindenylmethylamine (modified prep.), b.p. 103—105°/4 mm. (hydrochloride, m.p. 211°), gives the HCO derivative, b.p. 190—195°/4.5 mm., which could not be cyclised. The Ac, b.p. 180—182°/4 mm., and Bz derivative, m.p. 115°, with POCl₃ in boiling PhMe or P₂O₅ in boiling xylene give 1-methyl- (I), b.p. 145—150°/20 mm. (methiodide, m.p. 114°; picrate, m.p. 211°; hydrochloride, m.p. 238—240°), and 1-phenyl-4:5-ethylene-3:4-dihydroisoquinoline, m.p. 52—54°, b.p. 204—206°/6 mm. (picrate, m.p. 181°; methiodide, m.p. 217—218°), respectively. Na-EtOH reduces (I) to 1-methyl-4:5-ethylene-1:2:3:4-tetrahydroisoquinoline, b.p. 110—120°/4 mm. (hydrochloride, m.p. 209—210°). Hydrind-1-one-3-acetic acid 2:4-dinitrophenylhydrazones melts at 242°. R. S. C.

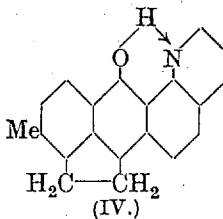
5:6- and 7:8-Benzolepidine.—See B., 1940, 642.

Chemotherapeutic studies in the acridine series. VII. Hydroxy- and chloroalkoxyderivatives of acridine. W. H. LINNELL and R. E. STUCKEY (Quart. J. Pharm., 1940, 13, 162—171; cf. A., 1938, II, 443).—3-Hydroxyacridone, m.p. 345—350°, obtained by refluxing 5-chloro-3-ethoxyacridine

with conc. HCl for 12—14 hr., yields 3-hydroxyacridine, m.p. 283—284°, on reduction (EtOH-Na) followed by oxidation of any 3-hydroxydihydroacridine formed by boiling with dil. FeCl₃ in HCl. The following are described: 4-, m.p. 162—163°, and 6-methoxy-4'-ethoxydiphenylamine-2-carboxylic acid, m.p. 174°; 9-methoxy-3-ethoxyacridine, m.p. 144°, -5:10-dihydroacridine, m.p. 90°, and -acridone; 5-chloro-7-, m.p. 175°, and -9-methoxy-3-ethoxyacridine, m.p. 164°; 3:9-dihydroxyacridine, m.p. 190—192°; 3:7-dihydroxyacridone, m.p. >350° (all m.p. corr.).

F. O. H.

20-Methyl-4-azacholanthrene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1940, 62, 1640—1645).—H₂-PtO₂ in 1:1 EtOAc-EtOH reduces 5- and 8-nitroquinoline (prep. described) to 5- (50%), m.p. 155—160° (decomp.) (Bz₂, m.p. 162.8—163.3°, and Ac₂ derivative, m.p. 115.5—116°), and 8-hydroxylaminquinoline (62%), m.p. 101—102° (decomp.) [picrate, m.p. ~120—125° (decomp.)], but complete hydrogenation in EtOH gives the 5-, m.p. 108—110°, b.p. 180—181°/7 mm., and 8-NH₂-derivative, m.p. 64—65°, b.p. 140.5—141.5°/7 mm. 5- (but not 8-)Cianoquinoline (I), m.p. 87—88°, b.p. 145—147°/7—8 mm., is obtained by a Sandmeyer reaction. 8-Cyanoquinoline, m.p. 82—83.5°, b.p. 137—140°/7 mm., is obtained from the Cl-compound by CuCN and a little MeCN in C₅H₅N at 200°. o-C₆H₄Me·MgBr and (I) give the ketimine, hydrolysed to 5-o-toluyloquinoline, m.p. 91.7—92.2° (not obtained from 5-bromoquinoline and o-C₆H₄Me·CN), which with a little Zn dust at 420—425° gives 4'-aza-1:2-benzanthracene [β -anthraquinoline, A., 1880, 262] (II), m.p. 170°. Li 7-methyl-4-hydrindenyl and (I) in boiling Et₂O-C₆H₆ give 17.5% of 7-methyl-4-hydrindenyl 5-quinolyl ketone, m.p. 135—135.5°, pyrolysed at 440° to 20-methyl-4-azacholanthrene (III) (12%), m.p. 184—185° [picrate, m.p. 288—290° (decomp.)]; s-C₆H₄(NO₂)₂ derivative, m.p. 175—176°. 7-Methyl-4-hydrindenyl 8-quinolyl ketone (similarly prepared), m.p. 135—135.6°, at 400—410°, best in presence of Pd-C, gives 50% of an unreactive substance [? (IV)], C₂₀H₁₅ON, m.p. 182—182.5°. M.p. are corr. R. S. C.



5- α -Methylbutyl-5-allylbarbituric acid and its 3-methyl derivative.—See B., 1940, 702.

Constitution of antipyrine and related compounds. VII. Complex bromine addition compounds of antipyrine. I. Knorr's dibromide. VIII. II. A. Sonn and W. Littler's antipyrine perbromide and T. Komata's four bromides. R. KITIMURA and G. SUNAGAWA (J. Pharm. Soc. Japan, 1940, 60, 60—65, 65—71).—VII. Knorr's "antipyrine 4:5-dibromide" (I) (A., 1887, 603) is OH·C·NPh \gg NMe}Br or, possibly, OB·C·NPh \gg NMe}Br. Antipyrine (II) absorbs only 2 Br from 0.01N-Br to give 4-bromoantipyrine (III). In H₂O (I) yields (II) by hydrolysis and in 0.1N-Na₂CO₃ liberates quantitatively 1 HBr. In warm

COMe₂ (I) gives COMe·CH₂Br and antipyrine hydrobromide (IV), but (III) is unaffected by COMe₂. 1 mol. of Br in CHCl₃ converts (IV) into (I) and a substance (V), m.p. 151—153°.

VIII. The structures of the bromides of Sonn *et al.* (A., 1933, 1306) and Komata (J. Chem. Soc. Japan, 1937, 58, 1202) are revised. The product, m.p. 159—161°, of Sonn *et al.* is identical with those, m.p. 171—172° and 165—166·5°, of Komata and is now assigned m.p. 162—163°. With H₂O it gives (IV), with COMe₂ gives (III), and is quantitatively debrominated by 0·1N-KOH; a structure is suggested. Komata's substance, m.p. 79—80°, is impure (III). The structure of the so-called pyrimidine tetra-bromide is also incorrect. R. S. C.

Polarisation in heterocyclic rings having aromatic character. IX. Friedel-Crafts reaction of basic, aromatic, heterocyclic [compounds]. E. OCHIAI [with T. MATSUWO, K. KOKEGUCHI, F. NAGASAWA, Y. TAMAMUSHI, K. UTAHASHI, H. TAKEUCHI, K. YANAI, and G. MASUDA] (J. Pharm. Soc. Japan, 1940, 60, 55—57).—1-Acetyl-2-methylindolizine, AcCl, and AlCl₃ in (CHCl₂)₂ give 1:3-diacetyl-2-methylindolizine (I). 2-Methylindolizine, AcCl (excess), and AlCl₃ in CS₂ [not (CHCl₂)₂] give a little (I). 2-Hydroxy-4-methylthiazole (Bz derivative, m.p. 104°) with BzCl and AlCl₃ in (CHCl₂)₂ gives 2-hydroxy-5-benzoyl-4-methylthiazole, m.p. 215—217°, but it does not react with BuⁿCl or Cl·[CH₂]₂·OEt in PhNO₂ or (CHCl₂)₂. 4-Chloro-2-methyl-5-ethoxymethylpyrimidine, C₆H₆, and AlBr₃ give 4-phenyl-5-benzyl-2-methylpyrimidine, m.p. 197°. No reaction (AlCl₃) occurs between AcCl and 4-methyl-[(CHCl₂)₂], AlCl₃ or SnCl₄], 2-phenyl-4-methyl-[(CHCl₂)₂], or 4-phenyl-glyoxaline [(CHCl₂)₂ or PhNO₂], 3:5-dimethylpyrazole (CS₂ or PhNO₂; no reaction with BzCl in C₅H₅N), 2-amino- [PhNO₂; gives the NHAc-derivative (II)], (II) (PhNO₂), 2- (PhNO₂) or 3-hydroxy-pyridine (PhNO₂), 1-methyl-2-pyridone [(CHCl₂)₂], 6-methyluracil [PhNO₂ or (CHCl₂)₂], or 2:4-diamino-6-methylpyrimidine. 2:6-Dichloro-4-methylpyrimidine, C₆H₆, and AlCl₃ or AlBr₃ do not react. R. S. C.

Glyoxalines (sulphanilamides).—See B., 1940, 642.

Phthalocyanines.—See B., 1940, 660.

Cyanines.—See B., 1940, 703.

2-Sulphanilamido-4-ethylthiazole. F. H. BERGEM, N. H. COY, and W. A. LOTT (J. Amer. Chem. Soc., 1940, 62, 1873—1874).—2-Amino-4-ethylthiazole, m.p. 35°, b.p. 118—120°/7 mm. (hydrochloride, m.p. 185·5—187·5°; Ac derivative, m.p. 117·5°), with *p*-NHAc·C₆H₄·SO₂Cl in C₅H₅N at 100° gives 2-*p*-acetamidobenzenesulphonamido-, m.p. 230·5—231°, and thence 2-sulphanilamido-4-ethylthiazole (I), m.p. 151—151·5° (hydrochloride, m.p. 226—228°; Na salt, m.p. 277·5—278°; Cu derivative). 2-*p*-Nitrobenzenesulphonamido-4-ethylthiazole (similarly prepared), m.p. 193—195°, is reduced to (I) by H₂—PtO₂. (I) and its Me analogue (II) have absorption max. at 262 (log ε 4·18) and 292 mμ. (log ε 4·30) and a min. at 263 mμ. (log ε 4·10). The toxicity of (I) greatly exceeds that of (II) or sulphathiazole. R. S. C.

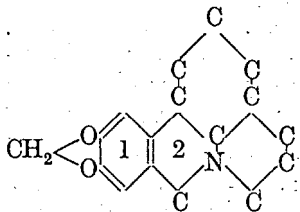
Bromoaneurin, m.p. 234° (decomp.), and aneurin monophosphate, m.p. 199°.—See A., 1940, III, 765.

Synthesis of thiazologlyoxaline derivatives. II. E. OCHIAI and F. Y. HOU (J. Pharm. Soc. Japan, 1938, 58, 33—34; cf. A., 1936, 1130).—Et 1-thiol-4-3'-pyridylglyoxaline-5-carboxylate, COMe·CH₂Cl, and NaOEt give Et 2-acetylthiol-4-3'-pyridylglyoxaline-5-carboxylate, m.p. 110—124°, converted by POCl₃ into Et 4-3'-pyridyl-4'-methylthiazolo-3':2'-1:2-glyoxaline-5-carboxylate, m.p. 138°. R. S. C.

4-Phenyl-2-(1'-benzthiazyl)thiolthiodiazole-5-thione.—See B., 1940, 686.

Semiquinones of oxazines, thiazines, and selenazines. S. GRANICK, L. MICHAELIS, and M. P. SCHUBERT (J. Amer. Chem. Soc., 1940, 62, 1802—1811).—Reductive titration (TiCl₃ or CrSO₄) shows formation in strong acid solution of stable semiquinonoid forms (containing a "free" valency) derived from phenoxazine (modified prep.), 3-hydroxy- and 9-amino-3-hydroxy-phenothiazine, 3:9-diamino- and 3-hydroxy-phenoxazine, and 3:9-bisdimethylaminophenselenazine. The results resemble those obtained (A., 1940, II, 110) for thionine and methylene-blue, but for the *as*-substituted compounds resonance cannot be "equivalent." Formation of colour without "equiv." resonance opens up possibilities with other types of compounds. Absorption spectra of the semiquinones are of two distinct types, a series of bands in the green or a broad band in the far blue; intermediate types are not met. R. S. C.

Erythrina alkaloids. VIII. Constitution of erythramine and erythraline. IX. Isolation and characterisation of erysodine, erysopine, erysocene, and erysovine. K. FOLKERS and F. KONIUSZY (J. Amer. Chem. Soc., 1940, 62, 1673—1677, 1677—1683; cf. A., 1940, II, 197).—VIII. Erythraline (I) contains 1 CH₂O₂, 1 OMe, and a *tert*. N, but no NMe, and absorbs 2 H₂ in presence of PtO₂ in H₂O containing a drop of HCl to give dihydroerythramine (II). Its methiodide, softens at 96—98°, m.p. 185—187°, and with KMnO₄ gives 4:5:1:2-CH₂O₂:C₆H₄(CO)₂NMe. The absorption spectra of (I), (II), and erythramine (III) resemble that of 6:7-methylenedioxy-1:2:3:4-tetrahydroisoquinoline hydrobromide, m.p. 255—256° (lit. 256—258°), but not that of hydrocotarnine. The annexed skeleton is probable for (I) and (II), the nature of rings 1 and 2 being proved.



IX. EtOH-extracts of seeds of *Erythrina* spp. contain, besides free (I), (III), erythratine, and hypaphorine (IV), larger amounts of physiologically active, H₂O-sol. substances, which by hydrolysis yield erysodine (V); m.p. 204—205°; [α]_D²⁵ +248° in EtOH, erysopine (VI), m.p. 241—242°; [α]_D²⁵ +265·2° in 6:4 EtOH-glycerol, erysocene (VII); m.p. 162°, [α]_D²⁵ +235·6°, and erysovine (VIII), m.p. 179·5°, [α]_D²⁵ +252·0°. (VI) is C₁₇H₁₉O₃N, contains 1 OMe and

2 (o)-phenolic OH, is unstable in alkali, and gives a green FeCl_3 colour. (V), (VII), and (VIII) are $\text{C}_{18}\text{O}_{21}\text{O}_3\text{N}$ and contain 2 OMe and one phenolic OH. (V), (VI), (VII), and (VIII) contain no NMe or CMe and are very weak bases. *E. abyssinica*, Lam., yields (IV) (0.6%), (V), and (VI). *E. sandwicensis*, Deg., yields (V), (VI), (VII), and (VIII). *E. glauca*, Wild., yields (V) and (VI). *E. Berteroana*, Urb., yields (IV) and (VIII). *E. americana*, Mill., yields (IV), (V), and (VII). *E. Poeppigiana* (Walp.), O. F. Cook, yields (IV), (V), (VII), and (VIII). *E. herbacea*, L., yields (IV) (0.5%), (V), and (VI). *E. flabelliformis*, Kearny, yields (IV) (1.2%), (V), (VI), (VII), and (VIII). Dil. HCl is preferable to alkali for the hydrolysis and some separation is possible by fractional hydrolysis. Names beginning "erythro" are used for alkaloids present as such; names beginning "eryso" are used for alkaloids liberated by hydrolysis from sol., natural precursors. R. S. C.

Morphimethine series. E. MOSETTIG (J. Org. Chem., 1940, 5, 401—415).— β -Methylmorphimethine, m.p. 136—137.5° [hydrochloride, m.p. 265—268° (vac.)], $[\alpha]_D^{25} + 323.6^\circ$ in H_2O ; benzoate, m.p. 145—147°, $[\alpha]_D^{25} + 260.1^\circ$ in H_2O , is reduced by Na and EtOH or, preferably, by Na-Hg in EtOH to dihydro- β -methylmorphimethine (I), m.p. 86—88.5° [hydrochloride (II), m.p. 235—236° (vac.) after softening at 233°, $[\alpha]_D^{25} - 86.3^\circ$ in H_2O ; benzoate, m.p. 162—164.5°]; the corresponding methiodide, m.p. 253—258° (decomp.), is converted by boiling Ac_2O into its Ac derivative, m.p. 265—270° (decomp.), $[\alpha]_D^{25} - 71.7^\circ$ in H_2O . (II) is hydrogenated (PtO_2 in abs. EtOH) to tetrahydro- α -methylmorphimethine hydrochloride (III), m.p. 230.5—232°, $[\alpha]_D^{25} - 35.6^\circ$ in H_2O . (II) is transformed by boiling AcOH containing 16% of HBr into acetyldihydromorphimethine (IV), m.p. 200—202.5° after softening at 196°, $[\alpha]_D^{25} + 118.4^\circ$ in CHCl_3 [hydrochloride (V), m.p. 270—280° (vac.)], $[\alpha]_D^{25} + 39.9^\circ$ in H_2O , which is hydrolysed (boiling N-NaOH) to dihydromorphimethine, m.p. 174—176°, $[\alpha]_D^{25} + 92.8^\circ$ in CHCl_3 [hydrochloride, m.p. 275—278° (vac.) after softening at 272°]. Ac_2O in $\text{C}_6\text{H}_5\text{N}$ appears to transform (IV) into an Ac_2 derivative which does not give a cryst. picrate or salicylate and is converted by HCl in EtOH or Et_2O -EtOH into (V). Dihydromorphimethine Me ether, an oil, gives a cryst. hydrochloride, m.p. 227—230° (vac.) after softening at 224°, $[\alpha]_D^{25} + 47.0^\circ$ in H_2O . The non-phenolic products of the demethylation of (I) contain an oily base which gives a hydrochloride, m.p. 229—230° (vac.) after softening at 224°, $[\alpha]_D^{25} + 13.56^\circ$ in H_2O , catalytically reduced (PtO_2 in abs. EtOH) to (III). Boiling AcOH containing 16% of HBr converts (III) into acetyltetrahydro- α -morphimethine, m.p. 240—242° (vac.) after softening at 237° [hydrochloride, m.p. 253—262° (vac.) after softening at 245°, $[\alpha]_D^{25} - 42.8^\circ$ in H_2O], which does not dissolve in cold 5% KOH. It is hydrolysed by boiling N-NaOH to tetrahydro- α -morphimethine (VI), m.p. 206—208° (vac.) after softening at 204° [hydrochloride, m.p. 243—249° (vac.) after softening at 240°, $[\alpha]_D^{25} - 29.6^\circ$ in H_2O], also obtained by the reduction (PtO_2 in abs. EtOH) of dihydromorphimethine. Diacetyltetrahydro- α -morphimethine is a non-cryst. compound which gives an oily

hydrochloride, picrate, and salicylate. (VI) and CH_2N_2 in MeOH yield tetrahydro- α -methylmorphimethine. Acetyltetrahydro- α -methylmorphimethine affords a hydrochloride, m.p. 240—245° (vac.) after softening at 232°, $[\alpha]_D^{25} - 47.53^\circ$ in H_2O . Morphine methiodide is converted by boiling AcOH into the Ac_2 compound, which is treated with AgOAc in boiling Ac_2O ; the filtrate from the pptd. Ag salts is heated at 170—180° and the product is acetylated, thereby giving a small proportion of an acetyl- β -morphimethine, m.p. 183—185° after softening at 182°. M.p. are corr. H. W.

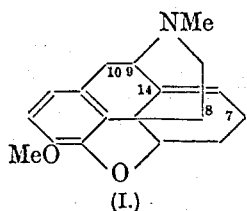
Halogeno-morphides and -codides and the mechanism of the morphine-apomorphine transformation. L. SMALL, B. F. FARIS, and J. E. MALLONEE (J. Org. Chem., 1940, 5, 334—349).—Hydrogenation (PtO_2 in glacial AcOH) of α -chlorocodide hydrochloride gives 52% of chlorodihydrocodide (I), m.p. 172.5—174°, $[\alpha]_D^{25} - 177.8^\circ$ in CHCl_3 [*d*-tartrate, m.p. 191—192° (decomp.)]; hydrochloride, m.p. 203—205° (vac.) and 226° after resolidification, $[\alpha]_D^{25} - 129.5^\circ$ in H_2O , 40% of tetrahydrodeoxycodine (II), and 7.5% of dihydrodeoxycodine-D (III). This relationship of α -chlorocodide (IV) to (I) leaves no doubt that Cl in (IV) is present at $\text{C}_{(6)}$. Similar reduction of β -chlorocodide (V) usually yields (II) and (III) with unchanged material. In HCl-EtOH nearly pure β -chlorodihydrocodide, m.p. $\sim 145^\circ$, $[\alpha]_D^{25} + 37.5^\circ$ in EtOH, is occasionally obtained. Reduction of bromocodide hydrobromide in glacial AcOH invariably gives (II) as main product. α -Chloromorphide and KI in dil. AcOH readily yield iodomorphide, $[\alpha]_D^{25} + 123.2^\circ$ in MeOH [hydriodide, $[\alpha]_D^{25} + 114.5^\circ$ in H_2O ; *H* tartrate, $[\alpha]_D^{25} + 120.3^\circ$ in H_2O ; salicylate, m.p. 161° (decomp.)], $[\alpha]_D^{25} + 113.4^\circ$ in EtOH; benzoate, m.p. 159—160° (decomp.), $[\alpha]_D^{25} + 115.5^\circ$ in EtOH; methiodide, $[\alpha]_D^{25} + 90^\circ$ to $+54^\circ$ in 36 hr.], which is converted by CH_2N_2 into iodicodide and is hydrogenated to a (?) bimol. base which could not be identified. β -Chloromorphide and KI in 10% AcOH give β -chloromorphide hydriodide, $[\alpha]_D^{25} \pm 0^\circ$ in H_2O , in 92% yield. The mother-liquors from the purification of (IV) after as complete removal of (IV) and (V) as possible give a 1:1 mol. compound of (IV) and (V), m.p. 115—117°, $[\alpha]_D^{25} - 150.4^\circ$ in abs. EtOH, also obtained by mixing equal quantities of (IV) and (V). Dihydro- ψ -codeine (VI) is transformed by PCl_5 in boiling CHCl_3 into 8-chlorodihydrocodide (VI), m.p. 123—124°, $[\alpha]_D^{25} - 42.7^\circ$ in abs. EtOH [tartrate, m.p. 230—232° (vac.)], obtained similarly but in poorer yield from dihydroallo- ψ -codeine (VII). It is unchanged by treatment with Na in EtOH or vigorous electrolytic reduction but is demethylated by NaOMe in MeOH at 140° to 8-chlorodihydro-morphide, m.p. 257—258° (vac.; decomp.). The mother-liquors from (VI) contain 1:8-dichlorodihydrocodide, m.p. 190.5—191.5°. Dihydrocodeine (VIII) and cold SOCl_2 yield 1-chlorodihydrocodeine, m.p. 187—190°, identified by reduction (Na and EtOH) to (VIII). Dihydroisocodeine (IX) similarly gives a Cl-base, m.p. 103—105° (tartrate), quantitatively reduced to the initial material. A Cl-base, m.p. 108—112°, is obtained from (VI), into which it is reconverted by reduction. (VII) yields chlorodi-

hydroallo-ψ-codeine, m.p. 189—191°; isolated through the *oxalate*. (VIII) and PBr_3 at 105—115° generally give compounds containing P but in an individual case (?) *6-bromodihydromorphide*, m.p. 260—262°, was isolated. (IX) gives an unidentified, halogen-free base isolated only as the *salicylate*. (VII) gives a small yield of *deoxymorphine-D*. A cryst. base, possibly *8-bromodihydrocodide*, m.p. 230—232°, is obtained from (VI). During the action of SOCl_2 on anhyd. morphine small amounts of β -chloromorphine (X) and *trichloromorphide*, m.p. ~195° (decomp.), $[\alpha]_D^{25} -285^\circ$ in MeOH (*hydrochloride*, $[\alpha]_D^{25} -245.6^\circ$ in H_2O), are produced. The last compound and CH_3N_2 afford *trichlorocodide*, m.p. 143—143.5°, $[\alpha]_D^{25} -302^\circ$ in EtOAc, the *hydrochloride*, $[\alpha]_D^{25} -218^\circ$ in H_2O , of which is hydrogenated (Pd— BaSO_4) to a non-cryst. base from which cryst. salts could not be obtained. Dichlorodihydrodeoxymorphine hydrochloride, m.p. 230—235° (lit. m.p. 270—272°), is transformed by boiling Ac_2O into *dichlorodiacetyldihydrodeoxymorphine*. The first step in the conversion of morphine into *apomorphine* (XI) is the formation of (X). The second intermediate is shown to be dichlorodihydrodeoxymorphine (XII). The first change involves the substitution of Cl for OH simultaneously with or followed by an α - γ shift of halogen. The cyclic ether group of (X), activated by the $\beta^{6:7}$ double linking, adds a mol. of HCl and the resulting (XII) undergoes rearrangement. The transitory intermediate is probably formed by loss of HCl at $\text{C}_{(8)}-\text{C}_{(14)}$ and an α - γ shift of the chain from $\text{C}_{(13)}$ to $\text{C}_{(8)}$ (aromatisation) to yield (XI).

Codeine, dihydro- ψ -codeine, (V), and α -chloromorphine are converted into resinous products by cold SO_2Cl_2 whereas morphine is unaffected. At 0° (IV) is rapidly transformed into *pentachloro-oxycodide*, $\text{C}_{18}\text{H}_{20}\text{O}_3\text{NCl}_5$, blackens at 180—200°, $[\alpha]_D^{25} -298.8^\circ$ in COMe_2 , which could not be hydrolysed or reduced to identifiable products.

H. W.

Deoxycodine studies. VI. Deoxycodine-D (deoxyneopine). L. SMALL and J. E. MALLONEE (J. Org. Chem., 1940, 5, 350—354).—8-Chlorodihydrocodide is very resistant to reduction but loses HCl under the prolonged action of Na in boiling cyclohexanol and gives *deoxycodine-D* [*deoxyneopine*] (I),



(I)

a liquid [*H d-tartrate*, m.p. 204—206° (vac.; decomp.), $[\alpha]_D^{25} \pm 0^\circ$ in H_2O ; *hydrochloride*, m.p. 234—235° (vac.), $[\alpha]_D^{25} -12.1^\circ$ in H_2O ; *H oxalate*, m.p. 220—221° (vac.; decomp.)]. Successive treatments of (I) in N-HCl with $\text{Br-H}_2\text{O}$ and SO_2 afford, probably, 1-bromodeoxycodine-D, m.p. 125—126°. (I) is hydrogenated (PtO_2) to dihydrodeoxycodine-D, m.p. 102—105°. (I) and MeI in EtOH yield the methiodide, m.p. 204—206° (vac.), transformed by boiling 20% NaOH into *deoxycodine-D-methine*, m.p. 76—77°; since this compound does not undergo the reaction characteristic of α - and γ -methylmorphimethines, (I) probably has the unsaturated linkings placed as shown. Support of this hypothesis is found in the observation

that (I) and CNBr give an amorphous Br-compound which slowly loses HBr whereas, under similar conditions, *deoxycodine-C* affords *cyanonordeoxycodine-C*, m.p. 159.5—161°. The mother-liquors from the prep. of (I) contain *deoxymorphine-D*, m.p. 254—255° (vac.; decomp.), also obtained in an individual experiment from dihydroallo- ψ -codeine and PBr_3 at 120° and easily converted by CH_3N_2 into (I). H. W.

Sinomenium and Cocculus alkaloids. XLVII. Alkaloids of *Stephania japonica*, Miers. VI. Protostephanine. II. H. KONDO and T. WATANABE (J. Pharm. Soc., Japan, 1938, 58, 46—51; cf. A., 1937, II, 475; 1939, II, 459).—Isolation of protostephanine (I), new formula, $(\text{OMe})_2\text{C}_{16}\text{H}_{10} > \text{NMe} + 1.5\text{MeOH}$, m.p. 75°, and “anhyd.”, m.p. 90—95°, α 0 [*platinichloride*, m.p. 223° (decomp.); *hydrochloride*; *methylmethosulphate*, sinters at 227°, m.p. 235°; *methiodide*, m.p. 220—221°], and of hasunohanine, m.p. 102—103°, is modified. Distillation of the aq. solution of the methohydroxide at 125°/vac. gives the oily methine (II) (*methiodide*, m.p. 185°); distillation of (II) in vac. gives an amorphous polymerisation product and NMe_3 . Ozonisation of (II) gives CH_2O ; Pd— C-H_2 (1 mol.) gives a syrup, b.p. 195—196°/0.05 mm. R. S. C.

Alkaloids, m.p. 105—106° (picrate, m.p. 332—334°), 114—116°, 105°, and 112°, phytosterol, and tannin, m.p. 254°, from bark of *Erythrophloeum guineense*, and alkaloids, m.p. 185—186° (picrate, m.p. 277—278°, acetate, m.p. 123—124°) and 122—124°, from the berries.—See A., 1940, III, 777.

Factors affecting halogen-metal interconversion. H. GILMAN and F. W. MOORE (J. Amer. Chem. Soc., 1940, 62, 1843—1846).—The rate of formation of $1-\text{C}_{10}\text{H}_7\text{Li}$ from $1-\text{C}_{10}\text{H}_7\text{Br}$ and RLi in the following solvents is $\text{Bu}^a_2\text{O} > \text{Et}_2\text{O} > \text{NPhMe}_2 > \text{C}_6\text{H}_6 > \text{cyclohexane} > \text{light petroleum}$ (b.p. 28—38°), is accelerated by Cu in C_6H_6 but not in C_6H_6 -light petroleum, varies with R thus: $\text{R} = \text{Pr}^a > \text{Et} > \text{Bu}^a > \text{Ph} > \text{Me}$ (very slight reaction), and is decreased by cooling to —80°. Coupling of radicals only rarely proceeds by way of an organo-metallic compound. Exchange of Cl in $1-\text{C}_{10}\text{H}_7\text{Cl}$ does not occur with LiBu^a or LiMe . PbPh_3Cl and EtBr (excess) give very rapidly a 98% yield of PbPh_4 . R. S. C.

Patterson analysis derived from the cyclol C_2 skeleton.—See A., 1940, I, 387.

Micro-determination of carbon and hydrogen. Use of Abrahamczik absorption tubes. R. O. CLARK and G. H. STILLSON (Ind. Eng. Chem. [Anal.], 1940, 12, 494—498).—Under ordinary analytical conditions, Abrahamczik type absorption tubes, with minor modifications, compare favourably with Pregl tubes in accuracy, ease of handling, and absorption capacity. They are unaffected by high or low humidity, temp. change, or keeping for long periods, and allow much time saving. The construction of the tubes, and all operations in the determination of C and H using them, are described in detail. J. D. R.

Determination of thiamin.—See A., 1940, III, 818.

A., II.—Organic Chemistry

NOVEMBER, 1940.

Oxidation of methane. III. T. OGAWA, A. MATSUI, H. NAGAI, and H. SENOO (J. Soc. Chem. Ind. Japan, 1940, 43, 116—117B; cf. B., 1938, 353).—The reaction $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$ is effected by passing CH_4 -air mixtures successively through Fe_2O_3 -MgO and Ni-kaolin catalysts in a Ni-Cr tube, at 1220°.

R. T.

Mechanism of polymerisation. IV. Experiments relating to the constitution of the solid dimeride and the liquid trimeride of $\beta\gamma$ -dimethylbutadiene, and to the separation of the higher polymerides. E. H. FARMER and J. F. MARTIN (J.C.S., 1940, 1169—1176).—The solid dimeride, $\text{C}_{12}\text{H}_{20}$, formed by the acid-catalysed (AcOH and 1.8 wt.-% H_2SO_4) polymerisation of $(\text{CH}_2\text{CMe})_2$ (cf. Farmer *et al.*, A., 1938, II, 79) yields with $\text{Pb}(\text{OAc})_4$ a mixture from which a monoacetate, b.p. 128—135°/12 mm., can be separated. This is hydrolysed to a ketone, $\text{C}_{12}\text{H}_{20}\text{O}$, m.p. 180° (oxime, m.p. 132°) (probably either 1:2:2:3-tetramethyl-1:3-endoethylenecyclohexan-5-one or 1:2:2:4-tetramethyl-1:4-endomethylenecycloheptan-6-one, but the 1:2:4- Me_3 compound is not excluded), purified through the semicarbazone, m.p. 255°. The ketone is oxidised (HNO_3) to a dibasic acid, $\text{C}_{12}\text{H}_{20}\text{O}_4$, m.p. 161°, and reduced (NaOEt - EtOH) to a hydrocarbon, m.p. 146°, probably 1:2:2:3-tetramethyl-1:3-endoethylenecyclohexane or 1:2:3:4-tetramethyl-1:4-endomethylenecycloheptane, although the 1:2:4- Me_3 compound is not excluded. Hydrogenation (PtO_2 - H_2) of the dimeride gives a dihydride, m.p. 78°, which is 1:2:2:3:4-pentamethyl-1:3-endoethylenecyclopentane or 1:2:2:4:5-pentamethyl-1:4-endomethylenecyclohexane, but the 1:2:4:5- Me_4 derivative is not excluded. The trimeric, tetrameric, and pentameric portions of the polymeride have been separated from each other by mol. distillation, leaving as a residue a highly viscous liquid of mainly hexameric complexity. Se-dehydrogenation of the trimeric portion gives an increased yield of the naphthalenic hydrocarbon (I) previously reported, and when the unattacked residue is submitted in the vapour phase to Pd-C-H_2 , an isomeric hydrocarbon, $\text{C}_{17}\text{H}_{22}$ [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 181°], is obtained. Oxidation ($\text{AcOH-H}_2\text{CrO}_4$) of (I) affords a quinone, $\text{C}_{17}\text{H}_{20}\text{O}_2$, m.p. 118°, probably a tetramethylisopropyl naphthaquinone. The trimeric fraction probably contains pentamethylisopropenyloctahydro naphthalene.

F. R. S.

Preparation of butadiene by catalytic hydrogenation of monovinylacetylene.—See B., 1940, 657.

Mechanism of Wurtz reaction.—See A., 1940, I, 415.

Mercury-photosensitised reactions of propane.—See A., 1940, I, 417.

Nitroparaffins.—See B., 1940, 657.

Leaf-alcohol. IV. *cis* and *trans* problem of leaf alcohol, the natural Δ^7 -hexenol. S. TAKEI, M. ONO, and K. SINOSAKI (J. Agric. Chem. Soc. Japan, 1940, 16, 772—780; cf. A., 1939, III, 536).—Hydrogenation ($\text{Pd-BaSO}_4\text{-H}_2$) of Δ^7 -hexenol (prepared from Δ^7 -hexenol by addition of Br and removal of HBr by KOH) in Et_2O at -18° yields *trans*- Δ^7 -hexenol, whilst in xylene at 100° the *cis*-isomeride (allophanate, m.p. 143°; 3:5-dinitrobenzoate, m.p. 28°; anthraquinone-2-carboxylate, m.p. 50°) is formed. Hydrogenation at 50° yields a mixture of the two isomerides. Contrary to Stoll and Rouvé (A., 1939, II, 2), leaf-alcohol is the *trans*-isomeride. J. N. A.

Preparation of higher unsaturated alcohols. V. Hydrogenation of methyl erucate. S. KOMORI (J. Soc. Chem. Ind. Japan, 1940, 43, 122—125B; cf. A., 1940, II, 202).—Hydrogenation of Me erucate ($\text{ZnO-Cr}_2\text{O}_3$ catalyst) affords chiefly docosenol, with a small quantity of behenyl alcohol and docosene. Erucyl and brassidyl alcohols and Δ^4 - and Δ^6 -docosenol are also formed in small amounts, probably by secondary isomerisation of docosenol.

R. T.

Synthesis of diisopropyl ether. X. Alcoholysis of diisopropyl sulphate with isopropyl alcohol. M. KATUNO (J. Soc. Chem. Ind. Japan, 1940, 43, 106—109B; cf. B., 1940, 591).— Pr^i_2O is prepared by the reaction $\text{Pr}^i_2\text{SO}_4 + \text{Pr}^i\text{OH} \rightarrow \text{Pr}^i_2\text{O} + \text{Pr}^i\text{HSO}_4$ (I). After Pr^i_2O has distilled off, H_2O is added to decompose (I), and the Pr^iOH formed is recovered.

R. T.

Mono-halogen derivatives of diethyl sulphone. L. RAMBERG and B. BÄCKLUND (Arkiv Kemi, Min., Geol., 1940, 13, A, No. 27, 50 pp.).— α -Bromo- (I), m.p. $2.5-3^\circ$, b.p. $124^\circ/8$ mm. (from $\text{SO}_2\text{Et-CHMe-CO}_2\text{H}$), β -bromo- (II), m.p. $19-20^\circ$, b.p. $153^\circ/8$ mm. (from PBr_5 and $\text{OH}[\text{CH}_2]_2\text{SO}_2\text{Et}$), and α -chloro-diethyl sulphone (III), m.p. 19.8° , b.p. $\sim 110^\circ/8$ mm. (from CHMeCl-SET), have been prepared. (I) and (II) are salted-in strongly by electrolytes (except KCl and NaCl), (II) having solubilities in *N-HI* and *N-HClO*₄ 97% and 117% > that in H_2O respectively. (I) and (II) are not attacked by KI or N_2H_4 , and (I) [but not (II)] is stable to acid AgNO_3 at 100° and NH_3 -Ag solutions at room temp. (I) [and similarly (III)] with excess of 2N-KOH at $90-100^\circ$ (very slowly at 25°) gives: $\text{CHMeBr-SO}_2\text{Et} + 3\text{OH}^- \rightarrow \text{cis-}\Delta^2\text{-butene (IV)} + \text{Br}^- + \text{SO}_3^{2-} + 2\text{H}_2\text{O}$. 85% of (IV), 75—81% of SO_3^{2-} , and 100% of Br^- (of the theoretical) are formed. The mechanism of the reaction is discussed. (II) with 0.25N-KOH at room temp. gives rapidly *Et*

vinyl sulphone, m.p. -13° to -12° , b.p. $106.8^{\circ}/9$ mm. (65% yield), which does not polymerise on storage at room temp., and gives with Br *Et* α -*tribromoethyl sulphone*, m.p. 64.8° . With EtSO_3Na (I) gives slowly $4\text{EtSO}_3\text{Na} \cdot \text{NaBr} \cdot \text{H}_2\text{O}$, decomp. $\sim 200^{\circ}$ (also prepared from EtSO_3Na and NaBr), whilst (II) gives $(\text{CH}_2 \cdot \text{SO}_2\text{Et})_2$. M. H. M. A.

Separation and identification of fatty acids. Y. INOUE and H. YUKAWA (J. Agric. Chem. Soc. Japan, 1940, 16, 504—512).—Fatty acids can be identified as hydroxamic acids which are prepared from the esters or glycerides by treatment at room temp. with NH_2OH in presence of NaOEt . The following *-hydroxamic acids* are described (m.p. in parentheses): *acet.* (88°), *propion.* (92.5 — 93°), *butyr.* (syrup), *hexo.* (63.5 — 64°), *octo.* (78.5 — 79°), *deco.* (88 — 88.5°), *dodeco.* (94°), *myrist.* (98 — 98.5°), *palmit.* (102.5°), *stear.* (106.5 — 107°), *arachid.* (109.5 — 110°), *behen.* (112.5°). The solubilities of the acids in EtOH , COMe_2 , Et_2O , H_2O , and light petroleum are recorded. The corresponding *hydroxamic acids* from oleic, linoleic, and linolenic acids have m.p. 61° , 41 — 42° , and 37 — 38° , respectively. The hydroxamic acids are converted into the original fatty acids by boiling with dil. H_2SO_4 — EtOH . J. N. A.

Direct esterification of higher fatty acids with glycerol. H. Synthesis of monolaurin. S. KAWAI and H. NOBORI (J. Soc. Chem. Ind. Japan, 1940, 110B; cf. A., 1940, II, 243).—Lauric acid (1 mol.) and glycerol (1.4 mols.) (30 min. at 240°) give monolaurin in 40% yield. R. T.

Action of sulphuric acid on petroselic acid. A. A. TSCHERNOJAROVA (J. Gen. Chem. Russ., 1940, 10, 146—149).—Petroselic acid treated consecutively with H_2SO_4 and H_2O yields ζ -*hydroxystearic acid*, m.p. 82° (*Et* ester, m.p. 45 — 46°). R. T.

Oxidation of ascorbic acid by oxygen with cupric ion as catalyst.—See A., 1940, I, 416.

Catalytic hydrogenation [of maleic and α -ketoglutaric acid] with deuterium.—See A., 1940, I, 416.

Indium oxalate and oxalatoindates.—See A., 1940, I, 418.

Production of formaldehyde by direct oxidation of methane. A. MATSUI and M. YASUDA (J. Soc. Chem. Ind. Japan, 1940, 43, 117—118B).— CH_4 -air-gaseous catalyst (HCl , SO_2 , Br , NO_2) mixtures are passed through tubes of various materials (Pyrex, SiO_2 , porcelain, Cu) containing solid catalysts (NaCl , KF , H_3BO_3 , U_3O_8 , BeO). The highest yields of CH_2O are obtained by Pyrex tubes, with NO_2 and U_3O_8 or BeO catalysts, at 600° . R. T.

Distillation of formaldehyde solutions.—See B., 1940, 657.

Photochemical decomposition of acetone.—See A., 1940, I, 417.

Diginin. I. C. W. SHOPPEE and T. REICHSTEIN (Helv. Chim. Acta, 1940, 23, 975—991).—Diginin, m.p. (indef.) 155 — 183° , $[\alpha]_D^{25} -223^{\circ} \pm 4^{\circ}$ in CHCl_3 , gives a well-defined Legal test but does not appear to be a lactone. It is very readily hydrolysed by dil.

mineral acids to *diginigenin* (I), $\text{C}_{21}\text{H}_{28}(\text{OH})_4\text{O}_4$, m.p. 115° , $[\alpha]_D^{25} -226^{\circ} \pm 3.5^{\circ}$ in COMe_2 , which does not contain OMe, and *diginose*, $\text{C}_7\text{H}_{14}\text{O}_4$, m.p. 90 — 92° , $[\alpha]_D^{25} +60^{\circ} \pm 1^{\circ}$ (final val. in H_2O), which gives the Keller-Kiliani reaction and contains 1 OMe. It is distinguished from cymarose since when oxidised and treated with $\text{NHPh} \cdot \text{NH}_2$ it gives a non-cryst. phenylhydrazide whereas cymaronephenylhydrazide (micro-prep. described) has m.p. 153.5 — 154° . (I) probably contains CHO since it readily affords a *semicarbazone*, m.p. 290 — 292° , and an *oxime*, thin prisms, m.p. 219 — 220° (decomp.), or octahedra, m.p. 235 — 236° (decomp.), strongly reduces $\text{Ag}_2\text{O} \cdot (\text{CH}_2 \cdot \text{NH}_2)_2$ at room temp., and gives a strong positive reaction with $1:4\text{-C}_{10}\text{H}_6(\text{OH})_2$. It contains 1 OH since on mild acetylation it affords a *monoacetate* (II) which becomes cloudy at 181° and melts to a clear liquid at ~ 185 — 200° , $[\alpha]_D^{25} -210^{\circ} \pm 4^{\circ}$ in COMe_2 [*monosemicarbazone*, m.p. 262 — 263° (decomp.)], which does not appear to contain further primary or *sec.* OH groups since it is relatively stable towards CrO_3 . Energetic acetylation of (I) leads to a *diacetate* (III), m.p. 177 — 178° (*monosemicarbazone*, m.p. 177 — 178°), which appears to contain an inert CO group or, less probably, a *tert.* OH since it is unchanged when warmed with strong acids. (I) contains a C:C linking since it and (II) give a distinct yellow colour with $\text{C}(\text{NO}_2)_4$ but this is not conjugated with CO since there is no selective absorption in the region of $240 \text{ m}\mu$. This is true also of (III). (I) is hydrogenated (PtO_2 in AcOH) to *tetrahydrodiginigenin* (IV), m.p. 229 — 231° , $[\alpha]_D^{25} +36.6^{\circ} \pm 1.5^{\circ}$ in CHCl_3 , which has no reducing properties, does not give a yellow colour with $\text{C}(\text{NO}_2)_4$, and does not react with $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ so that $\cdot\text{CHO}$ has been reduced. The presence of inert $\cdot\text{CO}$ is shown by the production under energetic conditions of an amorphous *oxime*, m.p. $\sim 132^{\circ}$. (IV) is transformed by short treatment with boiling Ac_2O into the *monoacetate* (V), m.p. 173 — 174° , $[\alpha]_D^{25} +38.8^{\circ} \pm 1.5^{\circ}$ in COMe_2 , also obtained by hydrogenation of (II). Prolonged treatment of (IV) with $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ at 100° affords non-cryst. *tetrahydrodiginigenin diacetate*. (III) is hydrogenated (PtO_2 in AcOH) to the non-cryst. *diacetate*, hydrolysed to (?) *hexahydrodiginigenin*, m.p. 207° , $[\alpha]_D^{25} -13.6^{\circ} \pm 2^{\circ}$ in CHCl_3 . Attempted partial reduction (Pd in EtOH) of (II) was unsuccessful whilst mild oxidation (CrO_3) of (V) yields an amorphous, neutral substance with aldehydic properties. Similar oxidation of (I) or (IV) leads to extensive degradation with production of acidic and neutral compounds from which only small amounts of homogeneous products can be isolated. Small amounts of CHI_3 are formed from (I) and OI' in MeOH . (I) and (IV) are stable to HIO_4 . It appears probable that (I) is a pregnane derivative. M.p. are corr. H. W.

***o*-Chlorophenylgentiobioside** [hepta-acetate, m.p. 207 — 208.5° (corr.), $[\alpha]_D^{25} -49.4^{\circ}$ in CHCl_3 ; heptapropionate, m.p. 178.5 — 179° , $[\alpha]_D^{25} -38.0^{\circ}$ in CHCl_3].—See A., 1940, III, 831.

Starch. II. Non-homogeneity of starch. K. H. MEYER, W. BRENTANO, and P. BERNFELD. III. Fractionation and purification of natural maize. K. H. MEYER, P. BERNFELD, and E. WOLFF. IV. Methylation and determination of terminal

groups of amylose and amylopectin of maize. K. H. MEYER, M. WERTHEIM, and P. BERNFELD. V. Amylopectin. K. H. MEYER and P. BERNFELD. VI. Acetates and nitrates of amylose and amylopectin. K. H. MEYER, P. BERNFELD, and W. HOHENEMSER. VII. Fine structure of the starch granule and the phenomena of swelling. K. H. MEYER and P. BERNFELD (Helv. Chim. Acta, 1940, 23, 845—853, 854—864, 865—875, 875—885, 885—890, 890—897; cf. A., 1929, 799).—II. Treatment of maize starch with H_2O at 70° or 80° or with 33% $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ at 20° removes $\sim 20\%$ of carbohydrates as limpid solution without causing destruction of the granules, which merely swell. The solutions slowly deposit a flocculent ppt. of amylose (I) which presents cryst. interferences and resists the action of β -amylase (II). If brought into solution by any means (I) is completely saccharified by (II). Prolonged action of the solvent removes $\sim 10\%$ of other fractions but the solutions are turbid and deposit ppts. more slowly or only after addition of precipitants. (II) does not cause complete saccharification but yields small amounts of residual dextrans which give a red colour with I, thus indicating the presence of amylopectin (III). The proportion of (I) varies from sample to sample. Starch therefore contains $\sim 20\%$ of a carbohydrate sharply differentiated from that retained in the swollen granule. The subdivision into (I) and (III) is therefore justified but it is proposed to distinguish (I) as a carbohydrate with non-branched mols. entirely saccharified by (II), and (III) as a carbohydrate with branched mols. degraded by (II) solely to residual dextrans. It should be noted, however, that only 20—30% of the maltose formed from starch by malt extract is derived from (I) whereas 70—80% is derived from (III) which suffers partial degradation. The product extracted by hot H_2O and consisting essentially of (I) is not homogeneous, the first fractions having a lower η and mol. wt. than the less sol. fractions.

III. Four fractions have been separated from crude (I), all of which are free from P. When dried at $105^\circ/\text{vac.}$ (I) is $\text{C}_6\text{H}_{10}\text{O}_5$ and does not show X-ray interferences. Over 54% H_2SO_4 (I) becomes $\text{C}_6\text{H}_{12}\text{O}_6$. Native (I) is sol. in H_2O at 70 — 80° but fractions obtained from it by crystallisation are very slightly sol. or insol. (I) pptd. from H_2O by EtOH is sol. in Et_2O . Insol. (I) can be converted into sol. (I) by dissolution in 33% $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and pptn. by COMe_2 . Sol. (I) does not present cryst. interferences; it loses its solubility after some hr. or days. The solubility of (I) in H_2O depends on its mol. wt., degree of purity, and size of crystallites. (I) migrates towards the anode. Its dissociation const. in 5×10^{-12} . (I) gives limpid solutions in warm $\text{HCO}\cdot\text{NH}_2$ but fractionated (I) readily gels in the course of a few hr. It is sol. in 33% $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, and $(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$ and in saline solutions which cause starch to swell. It dissolves rapidly in 1% NaOH but a gel of the Na compound is rapidly formed. It gives a blue colour but does not dissolve in $\text{CuO}\cdot\text{NH}_3$. It has $[\alpha]_D +195$ — 197° in H_2O , $+152^\circ$ in $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ (calc. for $\text{C}_6\text{H}_{12}\text{O}_6$). The various fractions are readily characterised by their η . The mol. wt. is 13,000—45,000.

IV. Starch or (III) becomes H_2O -sol. when pptd. from 33% $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and then give 3% solutions in 1% NaOH , in which they are readily methylated. (II) is sol. in dil. alkali and can be methylated directly. Methylation and hydrolysis gives 3.5%, 0.32%, and 3.7% of tetramethylglucose from starch, (I), and (III), respectively. (II) has one terminal group for ~ 300 residues whereas starch and (III) have one group for ~ 30 or 27 residues. As the mol. wt. of the sample of (I) was $\sim 50,000$ and mean degree of polymerisation 300, (I) has only one terminal group per mol., which is not branched. (III) has >50 ramifications of its chain. A single treatment of (I) affords dimethyl-amylose, which is sol. in H_2O , CHCl_3 , and COMe_2 , does not give a blue colour with I, and is appreciably less viscous than trimethylamylose (IV) in CHCl_3 . (IV) differs widely from trimethylstarch and trimethyl-amylopectin (V), more particularly in its ability to form films and threads. The η of (IV) in CHCl_3 is \gg that of a branched product of the same mol. wt. and increases less rapidly with concn. than that of (V). The presence of CHO at the other end of the mol. of (I) is established by means of Ag_2O ; Fehling's solution is not sufficiently sensitive. This appears true of (III) also. Electrodialysis does not affect (IV) or (V).

V. Starch is dissolved at room temp. by $(\text{CH}_2\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, which may possibly cause hydrolysis, and also by 33% $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$, conc. $\text{CCl}_3\cdot\text{CO}_2\text{Na}$, $\text{CCl}_3\cdot\text{CO}_2\text{H}$, and $\text{CS}(\text{NH}_2)_2$ with which hydrolysis may be regarded as impossible. The linkings ruptured under these conditions can only be caused by secondary valencies. These facts combined with the observation that (III) separated from aq. solution has the same cryst. interferences as (I) suggest that the giant branched mols. are united one to the other at numerous points by little cryst. micelles representing associations of parts of the chains; inversely, the cryst. micelles are united by loose reticules constituted by parts of the chains not arranged in nets, by mol. threads. (III), pptd. by COMe_2 from $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$, is free from P and readily sol. in warm H_2O when fresh. This solubility is rapidly lost when it is dried. Aq. solutions soon become cloudy and deposit (III) quantitatively after several days. They give a pure blue colour with I. In an electric field (III), even when free from P, is transported to the anode, where it is deposited as a gel. After desiccation (III) is practically insol. in H_2O but the particles still swell somewhat in hot H_2O , thereby differing from (I). (III) can be separated into fractions of increasing mol. wt. and diminishing solubility. The simpler fractions are pptd. as flocks by COMe_2 ; the higher fractions form only viscous masses. Only the acetates of the former are sol. in CHCl_3 or CCl_4 . (III) is converted by (II) into maltose and residual dextrin-I (VI) which gives a red colour with I. The terminal groups not affected by this enzyme are attacked by α - (but not by β -)glucosidase (VII) with formation of glucose. The branching linkings are thus of the α -1:6-type; the disaccharide which is the basis of the ramifications is α -gentiobiose, probably identical with Croft Hill's revertose and Fischer's isomaltose. By the prolonged action of (VII) (VI) is converted into residual dextrin-II, which is transformed by (II) into maltose and residual

dextrin-III, which is coloured brown-red by I, thus resembling glycogen. The observations are incompatible with the formulæ of Staudinger and Husemann or Hirst and Young and a new scheme is suggested.

VI. (I) is readily converted into its *triacetate* (VII), which is more freely sol. than cellulose triacetate and differs considerably from the acetates of starch and (III), giving very solid films which can be drawn into resistant threads. *Amylopectin triacetate* (VIII) from crude (III) is sol. in $C_2H_2Cl_4$, in which acetates from fractionated (III) are insol. The viscosity-concn. graphs of (VII) and (VIII) differ sharply from one another. This appears also true of the *nitrates* of (I) and (III).

VII. The sub-microscopic structure of the starch grain and the processes of swelling, crystallisation, and gel formation are discussed. H. W.

Nature of bonds in starch. C. E. H. BAWN, E. L. HIRST, and G. T. YOUNG (Trans. Faraday Soc., 1940, 36, 880—885).—Kinetic experiments on the disaggregation of methylated starch support other evidence in indicating that the linking between repeating units (each of 24—30 glucose units) is of the normal glucosidic type and not due to H-bonding. On the other hand the pasting of native starch with hot H_2O and its subsequent pptn. in granular form are consistent with the formation of H bonds between the macromols. F. L. U.

Carrageen mucilage. E. G. V. PERCIVAL and J. BUCHANAN (Nature, 1940, 145, 1020—1021; cf. A., 1940, II, 245).—Haas' view (A., 1921, i, 839) that the polysaccharide obtained by extraction of carrageen moss with hot H_2O is essentially the Ca salt of a carbohydrate ethereal sulphate has been confirmed. Attempted acetylation ($C_5H_5N + Ac_2O$) on the hot and other extracts was unsuccessful. Hydrolysis yielded a mixture of sugars containing ~50% of galactose, which appears to be the main unit of the mol. Direct methylation of the hot extract is difficult, and gives a OMe content ~15%. Hydrolysis followed by acetylation and vac. distillation gave a dimethylhexose triacetate (~40%) and a monomethylhexose tetra-acetate (~20%), both of which yielded tetramethylgalactopyranoseanilide on suitable treatment. Deacetylation followed by osazone formation gave 6-methyl-*d*-galactosazone and *d*-galactosazone, respectively. L. S. T.

Iodine reaction of glycogen and starch in presence of adrenaline. P. MARQUARDT (Klin. Woch., 1939, 18, 1396—1397). M. K.

Cyanic acid. IV. Constitution of cyanic acid. Carbamyl fluoride and bromide. M. LINHARD and K. BETZ (Ber., 1940, 73, [B], 177—185; cf. A., 1938, I, 517; II, 352).—On electronic grounds, the structure of cyanic acid (I) is regarded as $H:N:C:O$; (acidic) H easily separates as H^+ , and the resulting $-N:C:O$ can electromerise into $N:C:O^-$. Liquid HF at -80° with H_2O -free Et_2O in a Cu vessel, and (I), give *carbamyl fluoride* (II), m.p. 47° , purified by sublimation at 20° /vac. on to a Cu rod at -80° (apparatus described). Dil. NaOH or aq. NH_3 hydrolyses (II) to cyanate and fluoride. With H_2O , (II) gives NH_4F ,

and thence NH_4HF_2 . Cryoscopically in dioxan, (II) shows normal mol. wt. HBr and (I) at -80° give *carbamyl bromide*, m.p. $27-27.5^\circ$, purified by sublimation, which is similarly hydrolysed by aq. NaOH. Metallic m.p. apparatus for use with (II) (m.p. determined by the fall of a Cu wire resting on the substance) is described. E. W. W.

Production of hydrocyanic acid and ammonia by the action of the high- and low-frequency electric arc on mixtures of nitrogen, carbon monoxide, and hydrogen at ordinary and low pressure.—See A., 1940, I, 417.

Aliphatic arsinic acids. II. Attempted preparation of di- and tri-arsinoacetic acids. A. R. MARQUEZ (Anal. Assoc. Quím. Argentina, 1940, 28, 82—86; cf. A., 1940, II, 208).— $CHCl_3 \cdot CO_2H$ or $CCl_3 \cdot CO_2Et$ with As_2O_3 in excess of NaOH yields only NaOAc and Na_3AsO_4 . F. R. G.

Redistribution reaction. R. D. STIEHLER and T. L. GRESHAM (J. Amer. Chem. Soc., 1940, 62, 2244).—Polemical against Calingaert *et al.* (A., 1940, II, 8). W. R. A.

Isomerisation of polymethylene hydrocarbons in presence of aluminium chloride. V. Isomerisation of *n*-amylcyclopentane. M. B. TUROVA-POLAK and G. A. TARASOVA (J. Gen. Chem. Russ., 1940, 10, 172—175; cf. A., 1940, II, 159).—*n*-Amylcyclopentane heated with $AlCl_3$ (20 hr. at $150-155^\circ$) yields 55% of cyclohexane derivatives (probably tetramethylcyclohexanes), together with cracking products of low b.p. R. T.

Catalytic dehydrogenation of representative hydrocarbons.—See A., 1940, I, 416.

Crystalline β -dihydrocarotene. P. KARRER and A. RUEGGGER (Helv. Chim. Acta, 1940, 23, 955—959).—Reduction ($Al-Hg$ in Et_2O) of β -carotene leads to β -dihydrocarotene, m.p. 182.5° , shown by its absorption spectrum to have 8 double linkings. Since it is biologically inactive it must be $(\cdot CH:CH \cdot CMe:CH:CH:CH \cdot CMe:CH:CH_2 \cdot C \begin{smallmatrix} \swarrow CMe_2 \cdot CH_2 \\ \searrow CMe-CH_2 \end{smallmatrix} > CH_2)_2$. H. W.

Heteropoly-acids as catalysts for vapour-phase partial oxidation of naphthalene.—See A., 1940, I, 416.

Sesquiterpenes. XLV. Synthesis of 1:4-dimethylazulene. P. A. PLATTNER and J. WYSS (Helv. Chim. Acta, 1940, 23, 907—911).— $o-C_6H_4Me \cdot CH_2Cl$ is converted successively into $o-C_6H_4Me \cdot CH_2 \cdot \dot{C}H(CO_2Et)_2$, $o-C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot CO_2H$, and 4-methylindanone, m.p. 96° . This is converted by the successive action of $MgMeI$, $KHSO_4$, and H_2 (Raney Ni) into 1:4-dimethylindane (I), b.p. $86^\circ/11$ mm. Treatment of (I) with $CHN_3 \cdot CO_2Et$ at $\sim 135-150^\circ$ followed by hydrolysis and distillation with Pd-C affords 1:4-dimethylazulene [additive compound, m.p. $177-178^\circ$, with $C_6H_3(NO_3)_3$; picrate, m.p. $142-143^\circ$]. All m.p. are corr. H. W.

Union of aryl nuclei. V. Modification of the Gomberg reaction. J. ELKS, J. W. HAWORTH, and D. H. HEY (J.C.S., 1940, 1284—1286; cf. A., II, 1938,

93).—Increased yields in the Gomberg reaction (A., 1926, 944) are obtained in certain cases by substituting NaOAc for NaOH; e.g., C_6H_6 and *o*-, *m*-, or *p*- $NO_2 \cdot C_6H_4 \cdot N_2Cl$ first at 5–10° and then at room temp. for 48 hr. give 45, 45, or 60% of 2-, 3-, or 4-nitrodiphenyl, respectively. *o*- $C_6H_4Cl \cdot N_2Cl$ or β - $C_{10}H_7 \cdot N_2Cl$ and C_6H_6 similarly afford increased yields (38 and 25%, respectively) of the respective diaryl derivative, but other diazotised amines give decreased yields (cf. also Hodgson *et al.*, A., 1940, II, 126).

[With S. E. LAWTON.] β - $C_{10}H_7 \cdot N_2Cl$ and $PhNO_2$ -aq. NaOAc give 2'- and 4'-nitro-2-phenylnaphthalene (total yield, 40%). A. T. P.

Action of selenium at high temperatures on gem-methylethyl groups. R. L. BARKER and G. R. CLEMO (J.C.S., 1940, 1277–1279; cf. A., 1937, II, 142).— $C_{10}H_8$ and α -methyl- α -ethylsuccinic anhydride in $AlCl_3$ - $PhNO_2$ afford β -1-naphthoyl- α -methyl- α -ethylpropionic acid, m.p. 135–136°, reduced (Clemmensen) to γ -1-naphthyl- α -methyl- α -ethylbutyric acid, b.p. 190°/1 mm., which is converted by H_2O - H_2SO_4 (1 : 3 vol.) at 100° (bath) into 1-keto-2-methyl-2-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (I), b.p. 170°/1 mm. (picrate, m.p. 85–86°). (I) is reduced (Clemmensen) to 2-methyl-2-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, b.p. 160°/1 mm. (picrate, m.p. 100–101°), dehydrogenated by Se at 280–300°, then 320°, to 2-methylphenanthrene (Et removed). (I) and $MgMeI$ afford 1-hydroxy-1 : 2-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, b.p. 150–160°/1 mm. (some dehydration occurs) (unstable picrate, m.p. 83–84°), converted by Se into 1 : 2-dimethylphenanthrene. A. T. P.

Synthetic oestrogens related to triphenylethylene. A. SCHÖNBERG, J. M. ROBSON, W. TADROS, and (in part) H. A. FAHIM (J.C.S., 1940, 1327–1329; cf. A., 1938, III, 908).—4 : 4'-Di-bromo- and -iodobenzophenone with $CH_2Ph \cdot MgBr$ yield β -phenyl- α -di-*p*-bromo-, m.p. 163–164°, and -iodo-phenylethyl alcohol, m.p. 198–199°, respectively, dehydrated (H_2SO_4 -AcOH) to β -phenyl- α -di-*p*-bromo-, m.p. 133–134°, and -iodo-phenylethylene, m.p. 155–156°, respectively. Bromination of (*p*- C_6H_4Hal)₂C:CHPh in AcOH yields β -bromo- α -di-*p*-chloro-, m.p. 156–157°, -bromo-, m.p. 164–165°, and -iodo-phenyl- β -phenylethylene (I), m.p. 173–174°. Of these $C_{20}H_{14}$ derivatives, only (I) induces some oestrogenic activity when injected subcutaneously in mice. (*p*-OMe- C_6H_4)₂C:CHPhBr (Koelsch, A., 1932, 848), however, is considerably more active than CPh_2 :CPhCl. 4 : 4'-Dimethoxystilbenediol diacetate is obtained by reduction (Zn dust, AcOH-conc. H_2SO_4 , ~40°) of anisil. A. LI.

Activation of aromatic halogen by ortho-ammonium salt groups. W. S. EMERSON, F. B. DORF, and A. J. DEUTSCHMAN, jun. (J. Amer. Chem. Soc., 1940, 62, 2159–2160).—2 : 4 : 6 : 1- $C_6H_2Br_3 \cdot NH_2$, 40% CH_2O , and Zn-Hg in boiling AcOH give 88% of *p*- $C_6H_4Br \cdot NMe_2$. Elimination of Br and methylation occur also with 4 : 2 : 6 : 1- $C_6H_2MeBr_2 \cdot NH_2$ (one Br removed), 3 : 2 : 4 : 6 : 1- $C_6H_2MeBr_3 \cdot NH_2$ [gives 3 : 4 : 1- $C_6H_3MeBr \cdot NMe_2$ (hydrochloride, m.p. 149–150°)], 2 : 4 : 6 : 1- $C_6H_2MeBr_2 \cdot NH_2$ [gives 2 : 4 : 1- $C_6H_3MeBr \cdot NMe_2$, b.p. 120–130°/20 mm. (hydrochloride, hygroscopic)], also obtained from 2 : 4 : 1-
S** (A., II.)

$C_6H_3MeBr \cdot NH_2$, and 2 : 4 : 6 : 1- $C_6H_2Me_2Br \cdot NH_2$. However, 2 : 4 : 6 : 1- $C_6H_2Cl_3 \cdot NH_2$ gives 2 : 4 : 6 : 1- $C_6H_2Cl_3 \cdot NMe_2$. R. S. C.

Restricted rotation in arylamines. I. Preparation and resolution of 3-bromo-2 : 4 : 6 : N-tetramethylsuccinanilic acid. R. ADAMS and L. J. DANKERT (J. Amer. Chem. Soc., 1940, 62, 2191–2193).—Mesidine, b.p. 225–226°, and Br in conc. HCl first at <15° and then at 100° (bath) give bromomesidine (82%), m.p. 40°, and thence bromo-N-methylmesidine (90%), b.p. 145°/15 mm. (purified by way of the NO-derivative; Ac derivative, m.p. 71°; obtained also less readily from 1 : 3 : 5 : 2- $C_6H_2Me_3 \cdot NHMe$), which with $(CH_2CO)_2O$ and a trace of H_2SO_4 in boiling C_6H_6 gives 3-bromo-2 : 4 : 6 : N-tetramethylsuccinanilic acid (I), 2 : 4 : 6 : 3 : 1- $C_6HMe_3Br \cdot NMe \cdot CO \cdot [CH_2]_2 \cdot CO_2H$, m.p. 136°. With brucine in $CHCl_3$, (I) affords the brucine salt, + $CHCl_3$, $[\alpha]_D^{25}$ –37.5° in EtOH, and thence the *l*-form, m.p. 132°, $[\alpha]_D^{25}$ –29° in EtOH, of (I); amorphous salt residues afford the *d*-form, m.p. 132°, $[\alpha]_D^{25}$ +27° in EtOH. Mutarotation is very slow, not occurring in aq. alkali or EtOH; in boiling BuOH the half-life is 9 hr. *l*- or *dl*-(I) gives the *dl*-Br₂-derivative, m.p. 171°. *dl*-, *l*-, and *d*-(I) with HNO_3 (*d* 1.5) at room temp. give the 3-bromo-5-nitro-derivatives, m.p. 165°, $[\alpha]_D^{25}$ 0, –6.3°, +6.0° in EtOH, respectively. 2 : 4 : 6 : N-Tetramethylsuccinanilic acid, m.p. 136°, with Br in CCl_4 gives (I). M.p. are corr. R. S. C.

Synthesis of 5-bromo-2-naphthylamine. H. GOLDSTEIN and K. STERN (Helv. Chim. Acta, 1940, 23, 818–820).—5 : 2- $C_{10}H_7Br \cdot CO_2Me$ is transformed by $N_2H_4 \cdot H_2O$ in boiling EtOH into 5-bromo-2-naphthylhydrazine, m.p. 214–215°, which yields 5-bromo-2-naphthazide, m.p. ~87° (much decomp.), converted by boiling Ac_2O into acet-5-bromo-2-naphthylamide, m.p. 165°. This is hydrolysed by boiling EtOH-conc. HCl to 5 : 2- $C_{10}H_7Br \cdot NH_2$, m.p. 58°. Et 5-bromo-2-naphthylcarbamate has m.p. 86°. M.p. are corr. H. W.

Radical of tri-*p*-tolylamine. S. GRANICK and L. MICHAELIS (J. Amer. Chem. Soc., 1940, 62, 2241–2242).—Potentiometric titration of (*p*- C_6H_4Me)₃N by $Pb(OAc)_4$ in 80% (vol.) AcOH and N_2 at 30° shows the blue product (Wieland, A., 1907, i, 1076) to be a singly charged cationic free radical, the absorption spectrum of which is determined. R. S. C.

Zwitterion structures in organic molecules.—See A., 1940, I, 403.

Preparation of amino-sulphonamides. E. MILLER, J. M. SPRAGUE, L. W. KISSINGER, and L. F. MCBURNEY (J. Amer. Chem. Soc., 1940, 62, 2099–2103).—*p*- $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot SO_2 \cdot NH_2$ with H_2 -PtO₂ or (better) -Raney Ni in EtOH gives *p*-toluidine- ω -sulphonamide, m.p. 171–172°. *p*- $NO_2 \cdot C_6H_4 \cdot [CH_2]_2 \cdot Cl$ and $CS(NH_2)_2$ (I) in EtOH give the isocarbamide, which with Cl_2 in H_2O gives *p*- $NO_2 \cdot C_6H_4 \cdot [CH_2]_2 \cdot SO_2Cl$, m.p. 81.5–83°, and thence (conc. aq. NH_3) β -*p*-nitrophenylethane- α -sulphonamide, m.p. 120.5–122°; reduced by H_2 -Raney Ni in EtOH to the *p*- NH_2 -amide, m.p. 181–182°. $ClSO_3H$ and $Ph \cdot [CH_2]_2 \cdot NHAc$ at –10°, later room temp., give *p*- β -acetamidoethylbenzenesulphonyl chloride, m.p. 142.5–144°, and

thence the *sulphonamide*, m.p. 168—169° (oxidised to $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$), hydrolysed by hot 1:3 $\text{HCl}\text{-H}_2\text{O}$ to *p*- β -aminoethylbenzenesulphonamide, m.p. 147.5—149° (hydrochloride, m.p. 228—230°). $p\text{-CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (prep. described), m.p. 166—167°, and $\text{H}_2\text{-Pd-C}$ in $\text{HCl}\text{-EtOH}$ give *benzylamine-p-sulphonamide*, m.p. 151—152° (hydrochloride, m.p. 249—250°; *Ac* derivative, m.p. 172—173°, also prepared from $\text{CH}_2\text{Ph}\cdot\text{NHAc}$ by ClSO_3H etc.). $p\text{-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ with (I) gives *S*- γ -cyanobenzylisothiocarbamide hydrochloride, m.p. 204—205°, and thence ($\text{Cl}_2\text{-H}_2\text{O}$) *p*-cyanotoluene- ω -sulphonyl chloride, m.p. 102—103°, and - ω -sulphonamide, m.p. 216—217°, and *p*-aminomethyltoluene- ω -sulphonamide, m.p. 160.5—162° [hydrochloride, m.p. 278—280° (decomp.)]. $\text{Cl}\cdot[\text{CH}_2]_3\text{-CN}$ gives similarly *S*- γ -cyanopropylisothiocarbamide hydrochloride, m.p. 125—127° (corresponding picrate, m.p. 163.5—164.5°), γ -cyanopropane-, m.p. 65—66°, and δ -amino-*n*-butane- α -sulphonamide (hydrochloride, m.p. 127—129°; *Bz* derivative, m.p. 154—155°). *S*- β -Cianoethylisothiocarbamide hydrochloride, m.p. 165—166°, $\text{CN}\cdot[\text{CH}_2]_2\cdot\text{SO}_2\text{Cl}$, b.p. 135—136°/5—6 mm. (sulphonamide, m.p. 94—95°), and γ -aminopropane- α -sulphonamide hydrochloride, m.p. 159—160°, are similarly prepared. β -Phthalimidoethane-sulphonyl chloride, m.p. 157.5—158.5°, and -sulphonamide, m.p. 207—208°, and thence (N_2H_4) $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{SO}_2\cdot\text{NH}_2$ (hydrochloride, m.p. 131—133°; *Bz* derivative, m.p. 165—166°) are prepared. $\text{CH}_2\text{Cl}\cdot\text{CN}$ and (I) in COMe_2 give *S*-cyanomethylisothiocarbamide hydrochloride, m.p. ~95—105° (decomp.), which is decomposed by $\text{Cl}_2\text{-H}_2\text{O}$. Separation of $\text{SO}_2\cdot\text{NH}_2$ or NH_2 of sulphanilamide from the *Ph* nucleus leads to inactive products. R. S. C.

Sulphanilamide derivatives.—See B., 1940, 762.

Substituted sulphanilamides. III. N^1 -Hydroxy- N^4 -acyl derivatives. M. L. MOORE, C. S. MILLER, and E. MILLER (J. Amer. Chem. Soc., 1940, 62, 2097—2099; cf. A., 1939, II, 308).— $\text{RCO}\cdot\text{NHPh}$ (1 mol.) and ClSO_3H (5 mols.), first at 5—20° and later at 55—65°, give acet., m.p. 147—148° propion-, m.p. 112—113°, *n*-butyr-, m.p. 118—119°, *n*-valer-, m.p. 111—112°, *n*-hexo-, m.p. 92°, *n*-hepto-, m.p. 85—86°, *n*-octo-, m.p. 69—70°, *n*-nono-, m.p. 72—72.5°, isobutyr-, m.p. 131—132.5°, isovaler-, m.p. 123—124°, and isohexo-, m.p. 78.5—79.5°, -amido-benzenesulphonyl chloride. With $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{C}_5\text{H}_5\text{N}$ or aq. Na_2CO_3 these give acet., m.p. 194—196°, propion-, m.p. 174—178°, *n*-butyr-, (I), m.p. 172—178°, *n*-valer- (II), m.p. 178—179.5°, *n*-hexo- (III), m.p. 175—179°, *n*-hepto- (IV), m.p. 166—169°, *n*-octo- (V), m.p. 160—163°, *n*-nono-, m.p. 168—172°, isobutyr-, m.p. 172—176°, isovaler-, m.p. 168.5—173°, and isohexo-, m.p. 153—157°, -amidobenzenesulphonylhydroxylamide. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ (VI), m.p. 170.5—173°, and *p*-nitrobenzenesulphonylhydroxylamide, m.p. 145—149°, unstable, are similarly prepared. $(\text{RCO})_2\text{O}$ and (VI) in EtOH give β -carboxy-propion-, m.p. 170—174°, and -acryl-amidobenzenesulphonylhydroxylamide, m.p. 184—185°, which are inactive against streptococci. Aq. NaOH hydrolyses (III) to *p*-*n*-hexoamidobenzenesulphinic acid, m.p. 113—116°, also obtained from the sulphonyl chloride by Na_2SO_3 . (I) and (V) are as active as, and (II), (III), and (IV)

more active than, sulphanilamide. BzCl and (VI) in $\text{C}_5\text{H}_5\text{N}$ or aq. Na_2CO_3 gave $p\text{-NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$. R. S. C.

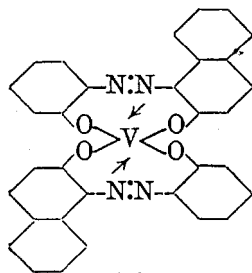
Oxidation of sulphanilic and arsanilic compounds by nascent hydrogen peroxide. G. BARKAN (Science, 1940, 92, 107).—Nascent H_2O_2 formed during the autoxidation of N_2H_4 in presence of Cu^{++} oxidises sulphanilamide (I) to blue-violet derivatives, extractable with $\text{C}_5\text{H}_{11}\cdot\text{OH}$ and BuOH etc. They are stable in these solvents, but not in H_2O , in which they change colour. Arsanilic acid (II) behaves similarly to (I). The blue-violet extracts in BuOH show absorption spectra practically identical in shape with a max. at ~590 μ , and the compounds from (I) and (II) are probably identical. L. S. T.

Action of nitrous acid on tertiary amines; influence of acidity. G. P. CROWLEY, G. J. G. MILTON, T. H. READE, and W. M. TODD (J.C.S., 1940, 1286—1289; cf. A., 1935, 337).—Concn. of mineral acid (H_2SO_4 , $\text{HBr} + \text{HCl}$, $\text{HBr} + \text{H}_2\text{SO}_4$) has a marked influence on yields of nitration, nitrosation, and fission products obtained from 4 mols. of NaNO_2 and 1 mol. of $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{-}p)_2$ in N_2 . It is confirmed that $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (I) is not formed in acid of concn. >3.9*N*. The nitration/nitrosation ratio, viz., amount of $\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NMe}_2\text{:}3\text{:}4]_2$ (II) : $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO-}p)_2$ (III), when (I) is not formed, does not increase as acid concn. increases (contrary to previous conclusions, *loc. cit.*). The above ratio is higher in solutions containing H_2SO_4 than in those containing HCl . In formation of (III) at low concn. of NaNO_2 , Me eliminated is converted into CH_3O , not into MeNO_3 (cf. *loc. cit.*). Mechanisms of reactions are not clear. The yield of (I) is less in H_2SO_4 or mixed acids than in HCl . In H_2SO_4 , the yield of (II) has a true max. even when 8 mols. of NaNO_2 are used, whereas in HCl the yield increases continuously as normality increases without giving a true max. For 4 mols. of NaNO_2 , the normalities at which (II) and (III) reach their max. are more widely spaced in H_2SO_4 or mixed acids than in HCl . With H_2SO_4 of high normality, a little $\text{CH}_2[\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{NMe}\cdot\text{NO-}3\text{:}4]_2$ is formed. Concn. of acid has little effect on yields of products from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$ and 3 or 6 mols. of NaNO_2 in 2.9—7*N*- HCl (excess), which give 3 : 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2$ (83%) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NMe}\cdot\text{NO}$ (~16%). At higher normalities of HCl , some 3 : 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHMe}$, 3 : 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}\cdot\text{NO}$, and 3 : 5 : 1 : 4- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Me}\cdot\text{NMe}\cdot\text{NO}$ are also formed. With $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMeEt}$, NaNO_2 , and 4*N*- HCl at 15°, Et is eliminated more easily than Me to give $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NO}$ (82.6%) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{NO}$ (17.4%). A. T. P.

Benzidine; m.p. study. C. WEYGAND (Z. ges. Naturwiss., 1937, 2, 408—409; Chem. Zentr., 1937, i, 4095).—Two metastable cryst. forms, m.p. 125° and 122°, are deposited from molten benzidine on cooling to ~100°. The stable form, m.p. 128°, is obtained at temp. nearer the m.p. All three forms, which are described in detail, coexist indefinitely at room temp. A. J. E. W.

Quadrivalent vanadium lakes of azo-dyes. H. D. K. DREW and F. G. DUNTON (J.C.S., 1940,

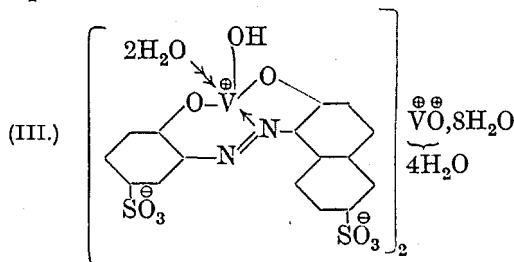
1064—1070; cf. A., 1940, II, 250).—Lakes of V^{IV} with azo-dyes containing reactive substituents (OH, NH₂, CO₂H) in *oo'*-positions with respect to ·N:N· are described. 1-*o*-Hydroxybenzeneazo-β-naphthol and 50% aq. vanadyl chloride-EtOH (reagent A)



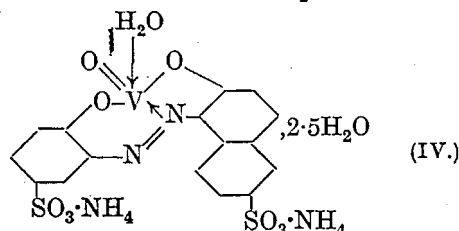
(I.)

afford the *bisazo-vanadi-complex* (I) (full quadrivalency used), stable to hot conc. HCl; use of moist vanadyl hydroxide-EtOH (reagent B) gives (I) and a *vanadyl complex*, C₁₆H₁₀O₃N₂V, 2H₂O (similar to Cr^{III} lakes) (loses 2H₂O at 130°; regains 1H₂O in moist air) (the corresponding C₅H₅N derivative,

C₅H₅N at 115° in dry air). 4-*o*-Hydroxybenzene-azoresorcinol and (B) afford the *vanadyl complex*, C₁₂H₈O₄N₂V, 2.5H₂O (aq. mineral acid liberates the azo-dye). 1-*o*-Carboxybenzeneazo-β-naphthol (as Na salt) and (A) give an impure *vanadyl complex*, C₁₇H₁₀O₄N₂V, 1.5H₂O (1 V : 1 azo-dye residue). No lake is obtained from 1 : 2-PhN₂·C₁₀H₆·OH. 1-*o*-Hydroxybenzeneazo-β-naphthylamine and (B) yield the anhyd. *bisazo-vanadi-complex*, C₃₂H₂₂O₂N₆V [similar to (I), but less stable to conc. HCl], and an unstable *vanadyl complex*, C₁₆H₁₁O₂N₃V, 2H₂O. Salicylidene-*o*-aminophenol and (B) afford a *vanadyl complex*, C₁₃H₉O₃NV (co-ordinatively unsaturated) [also + C₅H₅N, NH₂Ph, (?) 6NH₂Ph, and COMe₂ (loses COMe₂ at 130°)]. 1,2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol or 1,2'-hydroxybenzeneazo-β-naphthol-6-sulphonic acid and (B) afford glassy complexes; aq. NH₃ or NaOH liberates ionised V and affords the Na salt, C₁₆H₉O₆N₂SV, 6.5H₂O, or NH₄ salt, C₁₆H₁₃O₆N₃SV, 7.5H₂O, of the respective vanadyl complexes. Similarly, 4,2'-hydroxy-5'-sulphobenzene-azoresorcinol gives the (NH₄)₂ salt, +5H₂O (loses 5H₂O at 145°; regains 2H₂O in moist air), and Na₂ salt, +7.5H₂O, of the vanadyl complex. 1,2'-Hydroxy-5'-sulphobenzeneazo-β-naphthol-6-sulphonic acid and (B) yield a *vanadyl salt* (III) of the vanadyl complex; unco-ordinated V is removed by aq. NH₃



(III.)



(IV.)

to give the (NH₄)₂ salt (IV). The derivatives of the azo-sulphonic acids are unstable to mineral acids and

cannot be prepared from (A) in absence of bases. Fastness properties to acids and alkalis of the dyeings with vanadyl lakes, although superior to those of the free dyes, are much inferior to those of the corresponding Cr^{III} lakes. Properties of the lakes suggest that the co-ordination no. of V^{IV} is 6. The stereochemistry of the vanadi- and vanadyl lakes may be regarded as identical with that suggested for the Cr^{III} lakes (cf. A., 1939, II, 309), V having octahedral symmetry.

A. T. P.

New aromatic fluoro-derivatives. III. (SRA.)

A. C. DE DEGIORGI and E. V. ZAPPI (Anal. Assoc. Quím. Argentina, 1940, 28, 72—81; cf. A., 1938, II, 482).—Diazotised 3 : 5-dibromo- and 3 : 4-dinitro-aniline with 40% HBF₄ yield the *benzenediazonium borofluorides*, decomp. 126° and 161°, respectively, which when heated give 1 : 3-dibromo-5-fluoro-, b.p. 204—206°/768 mm., and 1-fluoro-3 : 4-dinitro-benzene, m.p. 34°, respectively. 1 : 3 : 5-NO₂·C₆H₃(OH)·OEt with Me₂SO₄-NaOH yields 3-nitro-5-ethoxyanisole, m.p. 43—44° (sublimes).

F. R. G.

Decomposition of *p*-hydroxybenzenediazonium salts by alcohols. H. H. HODGSON and C. K. FOSTER (J.C.S., 1940, 1150—1153).—Cameron's results (A., 1898, i, 364) on the decomp. of *p*-OH·C₆H₄·N₂Cl (= A) by MeOH and EtOH are confirmed. Decomp. of the salt 2A, ZnCl₂ (I) with MeOH or EtOH also gives PhOH (38.4%); some (*p*-OH·C₆H₄·N₂)₂ (II) (identified as diacetate or Br₄-derivative) is also formed. Decomp. of (I) with MeOH or EtOH in presence of ZnO affords PhOH (60—63%) and less (II); MeOH-NaOMe gives PhOH (22%) and much (II), whilst Bu^oOH-Zn dust at 30° gives PhOH (35.7%) and (II) (58.5%). (I)-MeOH-Br give bromo-anil and (mainly) 2 : 4 : 6 : 1-C₆H₂Br₃·OH. Decomp. of (I) in presence of excess of HCl also increases the yield of PhOH. Mechanisms of reaction are discussed; oxonium salt formation at the phenolic OH is probably the reason why this group behaves similarly to NO₂ in the above decomp. The salt 2*p*-OMe·C₆H₄·N₂Cl, ZnCl₂ resists a similar decomp. with MeOH, but in presence of Zn dust some PhOMe is formed. (I) is stable when dry and more convenient to use than (A).

A. T. P.

Migration of halogen [*para* to hydroxyl] in a derivative of *m*-cresol. A. B. SEN (Proc. Nat. Acad. Sci. India, 1939, 9, 89—92).—3 : 4 : 1-C₆H₃MeBr·OH (prepared from *m*-C₆H₄Me·NH₂ via 3 : 4 : 1-C₆H₃MeBr·NHAc or from *m*-cresol) with AcOH-HNO₃ (*d* 1.4) yields 4 : 6 : 3 : 2 : 1-(NO₂)₂C₆HMeBr·OH (I), m.p. 115° (cf. Walther *et al.*, A., 1915, i, 879) (*p*-toluenesulphonate, m.p. 141°), identical with that prepared by Sane *et al.* (A., 1928, 1130). 2-Bromo-4 : 6-dinitro-3-methyldiphenylamine, m.p. 130°, is obtained from 1 : 3 : 2 : 4 : 6-C₆HMeClBr(NO₂)₂ [prep. from (I) and *p*-C₆H₄Me·SO₂Cl·NPhEt₂] and NH₂Ph in EtOH + NaOAc.

A. Li.

Halogeno-4-alkylphenols.—See B., 1940, 762.

Nitrosation of phenols. XVIII. Synthesis of 3-fluoro-4- and -6-nitrosophenol. Comparison of the stabilities of 3-halogeno-4-nitrosophenols. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1940,

1268—1271; cf. A., 1940, II, 135).—1:3:4-OH·C₆H₃F·NO₂ and Me₂SO₄·K₂CO₃ give 1:3:4-OMe·C₆H₃F·NO₂, reduced by Fe-HCl-EtOH to 3-fluoro-4-aminoanisole, m.p. 50°, converted by Caro's acid into 3-fluoro-4-nitrosoanisole, m.p. 46°, and thence by HCl (*d* 1.16)—MeOH into 1:3:4-OH·C₆H₃F·NO (I), m.p. 161° [Co salt, m.p. 130—140°, not co-ordinated], obtained also from *m*-C₆H₄F·OH·C₅H₅N·NO·SO₄H at <10°. (I) is probably a NO-compound rather than a quinoneoxime; it is more stable than other 1:3:4-OH·C₆H₃Hal·NO. (I) could not be methylated nor converted into 3-fluorobenzoquinone-4-oxime. 1:3:6-OMe·C₆H₃F·NH₂ (Ac derivative, m.p. 132°) and Caro's acid afford 3-fluoro-6-nitrosoanisole, m.p. 150°, and thence (H₂SO₄—MeOH) the *-phenol* (does not melt; does not condense with NPhMe₂) [Co(NO₃)₂—aq. MeOH give a co-ordinated Co salt, m.p. ~105°, also obtained from *m*-C₆H₄F·OH—aq. H₂SO₄—Na₃Co(NO₂)₆]. A. T. P.

Kinetics of oxidation of 2:6-dinitrophenol by potassium permanganate.—See A., 1940, I, 415.

Dehydrogenation. III. Formation of naphthols from alcohols and ketones of the tetrahydronaphthalene group. R. P. LINSTAD and K. O. A. MICHAELIS (J.C.S., 1940, 1134—1139).—Dehydrogenation in the liquid phase, best using Pd-C prepared in dil. solution, of 1-keto-1:2:3:4-tetrahydronaphthalene (I) (46%; in *p*-cymene), *ar*- (55) (quickly dehydrogenated) and *ac*-tetrahydro-β-naphthol (60; in mesitylene), *trans*-α- (19) and *cis*- (28) and *trans*-β-keto-decahydronaphthalene (II) (41; in *p*-cymene), and *cis*- (12) and *trans*-decahydro-β-naphthol (17; only 7% in *p*-cymene), gives the respective C₁₀H₇·OH (yield quoted) and C₁₀H₈. (II) also affords some (2-C₁₀H₇)₂. Ketones are more readily dehydrogenated than alcohols, and *cis*- more readily than *trans*-compounds. Drastic conditions (leading to elimination of O) are needed to dehydrogenate the substances furthest removed from the aromatic type. Tetrahydronaphthalene is readily dehydrogenated in the liquid phase only when boiling. Rapid catalytic dehydrogenation is effected when the liquid boils at 185° under reduced pressure or on addition of diluent (mesitylene), but none in the tranquil liquid at ~200°. 4-Keto-1:2:3:4-tetrahydrophenanthrene (in *p*-cymene) is dehydrogenated at 240° to 62% of 4-phenanthrol (cf. Mosettig *et al.*, A., 1937, II, 145), phenanthrene, and a compound, m.p. 312°. A. T. P.

Synthesis of dihydrodiethylstilboestrol. A. M. DOCKEN and M. A. SPIELMAN (J. Amer. Chem. Soc., 1940, 62, 2163—2164).—Contrary to Dodds *et al.* (A., 1939, II, 312; cf. A., 1940, II, 79), hydrogenation (Pd-C, prepared by Hartung's method; Raney Ni; or Cu chromite) of (*p*-OMe·C₆H₄·CET)₂ or of (*p*-OH·C₆H₄·CET)₂ (Raney Ni; EtOH) gives only the stereoisomeride of low m.p. The crude product obtained from anethole and HBr (not HCl) in light petroleum (cf. Orndorff *et al.*, A., 1900, i, 289) with Mg (not Na) in boiling Et₂O gives (*p*-OMe·C₆H₄·CH₂Et)₂ m.p. 146° (with polymerides and a little of the isomeride, m.p. 56°); converted by KOH—EtOH at 225° into (*p*-OH·C₆H₄·CH₂Et)₂, m.p. 185—186° (over-all yield 10—15%). R. S. C.

Dibenzofuran [diphenylene oxide]. XIX. Derivatives of 2:2'-dihydroxydiphenyl. H. GILMAN, J. SWISS, and L. C. CHENEY (J. Amer. Chem. Soc., 1940, 62, 1963—1967; cf. A., 1940, II, 187).—(*o*-OH·C₆H₄)₂ [prep. in 28.6% yield from dibenzofuran (I) by KOH—NaOH at 400—410°], m.p. 108—109°, and 10% NaOH—Me₂SO₄ give 87% of (*o*-OMe·C₆H₄)₂, m.p. 154—155°. With LiBu⁺ in Et₂O this gives the 3:3'-Li₂ derivative (II), the structure of which is proved by conversion by Me₂SO₄ into (2:3:1-OMe·C₆H₃Me)₂ and by O₂ into 3-hydroxy- (32.2%), m.p. 115—116°, and 3:3'-dihydroxy-2:2'-dimethoxydiphenyl (1.42%), m.p. 174.5—175.5° [derived (OMe)₂-compound (III), m.p. 104—105°]. With CO₂, (II) yields 2:2'-dimethoxydiphenyl-3:3'-dicarboxylic (IV) (49.9%), m.p. 208—209° (Me₂ ester, m.p. 76—77°), and 3-carboxylic acid (9.3%), m.p. 114.5°. Demethylation of (IV) by HI gives 2:2'-dihydroxydiphenyl-3:3'-dicarboxylic acid, m.p. 304° (decomp.), which with HBr (*d* 1.49) or ZnCl₂ at 240—250° gives only (I). Veratrole (V) and LiBu⁺ in Et₂O give the 3-Li derivative [with CO₂ affords 2:3:1-(OMe)₂C₆H₃·CO₂H], which with CuCl₂ in boiling Et₂O—C₆H₆ affords (III) (1.8%) and (V) (63.5%). The product of Diels *et al.* (A., 1902, i, 219) is 5:5'-dibromo-2:2'-dihydroxydiphenyl (VI) (diacetate, m.p. 105—106°; *p*-toluenesulphonate, m.p. 198—199°), since with Me₂SO₄—NaOH it gives its Me₂ ether (VII), m.p. 130—131°, which is also obtained from 5:1:2-C₆H₃BrLi·OMe by CuCl₂. LiBu⁺ in Et₂O—C₆H₆ converts (VII) into the 5:5'-Li₂ derivative, which yields [2:5:1-OMe·C₆H₃(CO₂H)]₂, m.p. 335—340° (decomp.). Br—AcOH and (VI) give 3:5:3':5'-tetrabromo-2:2'-dihydroxydiphenyl [previously (*loc. cit.*) unoriented], m.p. 200—201°, the Me₂ ether, m.p. 86—87°, of which with LiPh—Et₂O, followed by CO₂, affords 5:5'-dibromo-2:2'-dimethoxydiphenyl-3:3'-dicarboxylic acid, sinters at 265°, m.p. 274—275° (decomp.), dehalogenated by H₂—Pd—CaCO₃ in EtOH at 3 atm. to (IV). R. S. C.

2-Methyl-1:4-naphthaquinol di-2:4:6-trimethylbenzoate, m.p. 204—205°.—See A., 1940, III, 820.

Derivatives of 1:2:3:4-tetrahydroxybenzene VI. Oxidation of quinol with sodium chlorate. W. BAKER and (MISS) I. MUNK (J.C.S., 1940, 1092—1093).—Quinol and aq. HCl—NaClO₃—OsO₄ at room temp./5 days afford 20% of a substance (I), (C₆H₆O₄)_n, m.p. 175—180° (decomp.) (sinters and darkens from 155°), or (rapid heating) darkens and melts ~185°, which is probably a dimeride of 2:3-dihydroxy-2:3-dihydrobenzoquinone (cf. Terry *et al.*, A., 1926, 1249). It is converted by boiling Ac₂O—NaOAc into 1:2:3:4-C₆H₂(OAc)₄, m.p. 134—136°, and thence by aq. KOH—EtOH—Me₂SO₄ into 1:2:3:4-C₆H₂(OMe)₄ [not obtained from (I)—Me₂SO₄—aq. KOH]. A. T. P.

Structure of metanethole. W. BAKER and J. ENDERBY (J.C.S., 1940, 1094—1098).—Anethole refluxed with 43% H₂SO₄ gives isonethole (I) (70%) and metanethole (II) (24% yield), similarly obtained from *p*-methoxy-α-methylcinnamic acid. (II) is one of the forms of 6-methoxy-1-*p*-anisyl-2-methyl-3-ethylhydrindene. (I) and H₂ (Pd—SrCO₃) afford the H₂-derivative, b.p. 187—188°/0.06 mm., converted by HBr (*d* 1.5)—AcOH into α-γ-di-*p*-hydroxyphenyl-β-

methyl-*n*-pentane. (II) with Br-AcOH gives a Br_2 -derivative, m.p. 135°, with HBr (*d* 1.5)-AcOH affords "metanethol" (6-hydroxy-1-*p*-hydroxyphenyl-2-methyl-3-ethylhydrindene), m.p. 156–157° (anhyd.) or ~83° (+ xH_2O), and with HNO_3 (*d* 1.4)-AcOH yields a $(NO_2)_2$ -derivative (III), m.p. 190°. (III) and aq. $KMnO_4$ -AcOH give 3-nitroanisic acid and 5(or 3)-nitro-2-(3'-nitroanisoyl)anisic acid, m.p. 221–222°. (II) and CrO_3 -AcOH- H_2SO_4 at 40° afford anisic and 2-anisoylanisic acid, m.p. 208°; the latter is prepared from 4:1:2- $OMe \cdot C_6H_3(CO)_2O$, $PhOMe$, and $AlCl_3$ at 80°. (I) and $SnCl_4$ - $CHCl_3$ (not HCl - $MeOH$) give (II) (10% yield), together, probably, with liquid stereoisomerides of (II). "Methronol" (Erdmann, A., 1885, 528) is probably 1-phenyl-2-methyl-3-ethylhydrindene. A. T. P.

p-Phenoxytriphenylmethane and the corresponding free radical. D. L. CLARKE and S. T. BOWDEN (J.C.S., 1940, 1334).—*p*- $OPh \cdot C_6H_4 \cdot COPh$ with $MgPhBr$ yields an oily carbinol (I) which gives a cryst. additive compound when the reddish-brown solution in liquid SO_2 is slowly evaporated. $AcCl$ or $HCl + CaCl_2$ in C_6H_6 or light petroleum converts (I) into the chloride, which with mol. Ag gives a deep orange colour, discharged by O_2 . Reduction (Zn dust in AcOH) of (I) yields *p*-phenoxytriphenylmethane, m.p. 142°. A. LI.

Interaction of β -ionone with halides in presence of lithium, and a synthesis of 1:6-dimethylnaphthalene. F. B. KIPPING and F. WILD (J.C.S., 1940, 1239–1242).— β -Ionone (I)- MeI - Et_2O added to Li - Et_2O (+ trace of $LiMe$) give δ -2:6:6-trimethyl- Δ^1 -cyclohexenyl- β -methyl- Δ^7 -buten- β -ol, b.p. 89–90°/0.2 mm. [ozonolysis product, geronic acid (II)], dehydrated ($KHSO_4$ at 135°, then at 170–180°/15 mm. in N_2) to δ -2:6:6-trimethyl- Δ^1 -cyclohexenyl- β -methyl- Δ^7 -butadiene (III), b.p. 113–115°/15 mm. [maleic anhydride gives a crude product, m.p. 155° (decomp.)]. Ozonolysis of (III) gives (II), whilst CrO_3 -aq. H_2SO_4 affords AcOH (1 mol.). Se dehydrogenation of (III) at 320–350° in a sealed tube gives 1:6- $C_{10}H_6Me_2$. (I) and $PhBr$ - Li - Et_2O (+ a trace of $LiPh$) afford δ -2:6:6-trimethyl- Δ^1 -cyclohexenyl- β -phenyl- Δ^7 -buten- β -ol, b.p. 147–150°/0.1 mm., converted by O_3 into (II). $CH_2=CH \cdot CH_2I$ and (I) afford a small amount of a distillable product, b.p. 139°/12 mm., containing no OH (cf. Karrer *et al.*, A., 1932, 852); the undistillable residue contains OH (Zerevitinov) but could not be dehydrated ($KHSO_4$) satisfactorily. $(CH_2)_2O$ and o - $C_6H_4Me \cdot MgBr$ at 0–10° give o - $C_6H_4Me \cdot [CH_2]_2 \cdot OH$ (phenylurethane, m.p. 82.5°); the bromide and $CHMe(CO_2Et)_2$ - $NaOEt$ afford Et β -o-tolylethylmethylmalonate, b.p. 184°/10 mm., and thence (20% KOH - $EtOH$) give β -o-tolylethylmethylmalonic acid, m.p. 138° (*p*-nitrobenzyl ester, m.p. 86°). The latter at 160–200° yields γ -o-tolyl- α -methylbutyric acid, b.p. 157°/0.12 mm. (slight decomp.), converted by conc. H_2SO_4 at 75–80° into 1-keto-2:5-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. 47° [2:4-dinitrophenylhydrazine, m.p. 219° (decomp.)], and thence by Zn -aq. HCl into 2:5-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 115°/14 mm., which with Se at 320–350° affords 1:6- $C_{10}H_6Me_2$,

identical with the dehydrogenation product of ionene. A. T. P.

Synthesis of phenylacetylenylhexylcarbinol [γ -hydroxy- α -phenyl- Δ^8 -noninene]. N. MALENOK and I. SOLOGUB (J. Gen. Chem. Russ., 1940, 10, 150–153).— $CPh:CH$ and heptaldehyde condense (Grignard) to phenylacetylenylhexylcarbinol, b.p. 144–145°/1 mm. (acetate, b.p. 147.5°/1.5 mm.), dehydrated by distillation from $H_2C_2O_4$ to α -phenyl- Δ^7 -nonen- Δ^8 -inene, b.p. 110–111°/1 mm. This is oxidised (AcO_2H) to $\gamma\delta$ -oxido- α -phenyl- Δ^8 -noninene, b.p. 133.5–134.5°/0.5 mm. R. T.

Enediols. IV. *cis-trans* Isomerism. R. C. FUSON, S. L. SCOTT, E. C. HORNING, and C. H. MCKEEVER (J. Amer. Chem. Soc., 1940, 62, 2091–2094; cf. A., 1940, II, 169).—Hydrogenation (PtO_2) of hindered $(COAr)_2$ for the min. time gives *cis*- $(\dot{C}Ar \cdot OH)_2$, but after a longer period gives the *trans*-compound, which is also obtained from the pure *cis*-form by H_2 - PtO_2 . The form of higher m.p. is assumed to be *trans*. The *trans*-form is more stable in air. Thus are obtained *cis*- (I), m.p. 123–124° (diacetate, m.p. 166–167°), and *trans*- $\alpha\beta$ -dihydroxy-2:6:2':6'-tetramethylstilbene (II), m.p. 151–152° (diacetate, m.p. 196–197°), *trans*- $\alpha\beta$ -dihydroxy-2:4:6:2':4':6'-hexa-ethyl-, m.p. 181.5–183.5°, and -methyl-stilbene, m.p. 157–165° (air), 166–168° (N_2). (I) and (II) give the same dibenzoate, m.p. 261–263° (uncorr.). 2:6:1- $C_6H_3Me_2 \cdot COCl$ gives (method: *loc. cit.*) 2:6:2':6'-tetramethylbenzil (III), m.p. 153–154°, and some benzoin, m.p. 127–128° [acetate, m.p. 104–105°; with $CuSO_4 \cdot C_5H_5N \cdot H_2O$ gives (III)]. Unless otherwise stated, m.p. are corr. R. S. C.

Polycyclic aromatic hydrocarbons. XXIV. J. W. COOK and R. H. MARTIN (J.C.S., 1940, 1125–1127).—A more detailed account of work previously reviewed (A., 1939, II, 413). Photo-oxides of the anthracene hydrocarbons are peroxides involving both *meso*-C atoms. Their formation appears to be unrelated to carcinogenic activity. 9-Methyl-, m.p. 122–123°, 10-methyl-, m.p. 129–130°, and 10-isopropyl-, m.p. 166–167°, 1:2-benzanthracene photo-oxides are prepared. 5:6:9:10-Tetramethyl-1:2-benzanthracene photo-oxide is unchanged by boiling 8% KOH - $EtOH$ for 2 hr. 9:10-Dimethyl-1:2-benzanthracene photo-oxide (I), m.p. 193–194°, or 188–189° (+ $1CHCl_3$), is hydrogenated (Pd -black, $COMe_2$; 20 hr. in the dark) to 9:10-dihydroxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene (Bachmann *et al.*, A., 1937, II, 497), but a similar hydrogenation (24 hr.) of (I) (+ $CHCl_3$), whereby HCl is probably liberated) affords (probably) 10-hydroxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene, m.p. 185°, converted by $MeOH$ - HCl into 9:10-dimethyl-1:2-benzanthracene. 1:2-Dimethylchrysene does not give a photo-oxide. A. T. P.

Acetylation of *d*- ψ -ephedrine and *l*-ephedrine. W. MITCHELL (J.C.S., 1940, 1153–1155).—Gentle acetylation (Ac_2O at 70°) of the corresponding bases gives acetyl-*d*- ψ -ephedrine, m.p. 103–104° (lit. 101°), $[\alpha]_D^{20} +110.0^\circ$ in $EtOH$ [hydrochloride, new m.p. 187°; hydrobromide (I), m.p. 181–182°], and acetyl-*l*-ephedrine (+ $2H_2O$), m.p. 52°, $[\alpha]_D^{20} +5.0^\circ$ in $EtOH$;

(anhyd.) m.p. 87°, $[\alpha]_D^{20} +7.0^\circ$ in EtOH. Since these compounds form NO-derivatives, they must be *O*-Ac derivatives (cf. Schmidt, A., 1914, i, 989): *nitroso-acetyl-d-ψ-ephedrine* (II) has m.p. 51–52°, $[\alpha]_D^{20} +148.0^\circ$ in EtOH, but the *l*-compound, m.p. ~85°, was not obtained pure. Hydrolysis (boiling aq. 5% NaOH) of (II) affords *nitroso-d-ψ-ephedrine*, m.p. 86°, $[\alpha]_D^{20} +124.5^\circ$ in EtOH, also obtained directly from the base, as is *nitroso-l-ephedrine*, m.p. 93°, $[\alpha]_D^{20} +80.5^\circ$ in EtOH. The compound described as “phenylmethylacetylaminobromopropane” (Schmidt, A., 1914, i, 989) has been shown to be (I). The equilibrium between *l*-ephedrine and *d-ψ-ephedrine* on heating with aq. HCl is discussed with particular reference to the hydrolysis of the acetylephedrine. M.p. are corr. F. R. S.

Local anaesthetics derived from tetrahydronaphthalene. Esters of [I] 2-dialkylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene, [II] 1-dialkylamino-2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. E. S. COOK and A. J. HILL (J. Amer. Chem. Soc., 1940, 62, 1995–1998, 1998–1999).—I. 1 : 4-Dihydronaphthalene (improved prep.) with, best, NaOCl–AcOH gives 26.5% of 2-chloro-3-hydroxy- (I) and with $\text{BzO}_2\text{H} \cdot \text{CHCl}_3$ affords 2 : 3-epoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (II) [also obtained from (I) by KOH–EtOH]. With the appropriate NHR_2 , (I) or (II) gives 2-diethylamino-, b.p. 138–145°/3 mm. [*hydrochloride*, m.p. 168–170°; *phenylurethane* (III), forms m.p. 125–126° and 79–80° (*hydrochloride*, m.p. 179–180°); *p-nitro*-, m.p. 110–111°, and *p-amino-benzoate*, m.p. 150–150.5°], 2-dibutylamino-, b.p. 155–157°/3 mm. [*phenylurethane*, m.p. 110–111° (*hydrochloride*, m.p. 198–200°); *benzoate hydrochloride*, m.p. 191–192°; *p-nitro*-, m.p. 157–160°, and *p-amino-benzoate*, m.p. 192–195°], and 2-piperidino-, new m.p. 51–52°, b.p. 170–172°/3 mm. [*hydrochloride*, m.p. 235–237°; *phenylurethane*, m.p. 81–82° (*hydrochloride*, m.p. 204–206° (decomp.)); *benzoate*, m.p. 154–156° (*hydrochloride*, m.p. 245–246°)], -3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. Of these products, (III) is the most potent local anaesthetic (rabbit's cornea), but is irritant.

II. 2-Bromo-1-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene and the appropriate NHR_2 give 1-diethylamino-, b.p. 181°/18 mm. [*benzoate hydrochloride*, m.p. 192–193°; *phenylurethane*, m.p. 104–104.5° (*hydrochloride*, m.p. 206–206.5°)], 1-di-n-butylamino-, b.p. 206–208°/17 mm., and 1-piperidino-, new m.p. 74–75° [*benzoate*, m.p. 81–82° (*hydrochloride*, m.p. 208–209° (lit. 176.5–177.5°)); *phenylurethane*, m.p. 145–146° (*hydrochloride*, m.p. 203–204°); *p-nitro-benzoate hydrochloride*, m.p. 238.5–239.5°], -2-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene. R. S. C.

Action of formic acid on triphenylmethyl ethyl ether and on triphenylmethyl chloride. S. T. BOWDEN and T. F. WATKINS (J.C.S., 1940, 1333–1334).—Reduction of $\text{CPh}_3 \cdot \text{OEt}$ to CHPh_3 by HCO_2H (measured by rate of evolution of CO_2 when the solid is added to anhyd. HCO_2H at $100 \pm 0.02^\circ$) is as rapid as that of $\text{CPh}_3 \cdot \text{OH}$, and more complete, whilst that of CPh_3Cl is complete but slower. A. LI.

α -Dihydro-theelin [-oestrone] from human pregnancy urine. M. N. HUFFMAN, D. W. MAC-

CORQUODALE, S. A. THAYER, E. A. DOISY, G. V. SMITH, and O. W. SMITH (J. Biol. Chem., 1940, 134, 591–604; cf. A., 1940, III, 582).—*Oestroneoxime O-carboxymethyl ether* (+0.5EtOH), m.p. 188° (obtained in quant. yield from oestrone, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NH}_2$, HCl, and KOAc in boiling Pr°OH), is sol. in aq. NaHCO_3 and hence is separable from non-ketonic oestrogens. *Oestriol 3-monobenzoate*, m.p. 225°, is oxidised by $\text{AcOH} \cdot \text{Pb}(\text{OAc})_4$ apparently to the corresponding dialdehyde. A micro-modification of the procedure of Whitman *et al.* (A., 1937, II, 289) is applied to the isolation (from urine collected during spontaneous labour and delivery) of small amounts of α -dihydrocestrone as its di- α -naphthoate. W. McC.

Sulphonated arylstearic acids.—See B., 1940, 724.

Attempted synthesis of papaverine. J. F. KEFFORD (J.C.S., 1940, 1209).—6-Nitro-3 : 4-dimethoxycinnamic acid, new m.p. 286° (decomp.), and FeSO_4 –aq. NH_3 afford the 6- NH_2 -compound (I), m.p. 175–177°, converted by conc. HCl into 6 : 7-di-methoxycarbostyryl, m.p. 229°. (I) gives (diazo-reaction) 6-cyano-3 : 4-dimethoxycinnamic acid, m.p. 273–274°, converted over Br in a desiccator into $\alpha\beta$ -dibromo-6-carboxy-3 : 4-dimethoxyphenylpropionic acid, m.p. 282°, and *cis*- ω -bromo-6-cyano-3 : 4-dimethoxystyrene, m.p. 155°. Mg veratryl bromide could not be prepared. A. T. P.

Synthesis of thyronine. C. R. HARRINGTON and R. V. P. RIVERS (J.C.S., 1940, 1101–1103).— $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ and $p\text{-C}_6\text{H}_4\text{Br} \cdot \text{OMe} \cdot \text{KOH} \cdot \text{Cu}$ -bronze at 150°, then 240°, give *Et* 4-*p*-methoxyphenoxybenzoate, m.p. 23–24°, converted by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in EtOH at 100° into 4-*p*-methoxyphenoxybenzhydrazide, m.p. 136–136.5° [*p*-toluenesulphonyl derivative (I), m.p. 172–173°]. (I) and $(\text{CH}_2\text{OH})_2 \cdot \text{Na}_2\text{CO}_3$ at 160° (1 min.) afford 4-*p*-methoxyphenoxybenzaldehyde (II), m.p. 60.5° (semicarbazone, new m.p. 212–213°). (II) and hippuric acid give the azlactone, converted by HI (*d* 1.7)– Ac_2O –red P into thyronine [4-*p*-hydroxyphenoxyphenylalanine] (cf. A., 1927, 961). Its *Me* ester *hydrochloride*, m.p. 215°, with $\text{NHET}_2 \cdot \text{BzCl} \cdot \text{C}_5\text{H}_5\text{N}$ yields ON-dibenzoylthyronine *Me* ester, m.p. 132–134°, with $\text{NHET}_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ gives N-*p*-toluenesulphonylthyronine, m.p. 141° (after sintering), and with CHCl_3 –aq. $\text{Na}_2\text{CO}_3 \cdot \text{ClCO}_2\text{CH}_2\text{Ph}$ at 0°, then at room temp., affords N-carbobenzoyloxythyronine, m.p. 105–106°. A. T. P.

Dialkylaminoalkyl furoates and benzoates as topical anaesthetics. E. S. COOK and C. W. KREKE (J. Amer. Chem. Soc., 1940, 62, 1951–1953).—The following are prepared. β -Diethylaminoethyl 2-furoate *hydrochloride*, new m.p. 130.4–131.9°, and *benzoate hydrochloride*, new m.p. 125.2–126.2°, and *hydrobromide*, m.p. 119.2–120.2°; γ -diethylamino-*n*-propyl 2-furoate *hydrochloride*, m.p. 132–134°, and *benzoate hydrochloride*, m.p. 110.9–114.9°, and *hydrobromide*, m.p. 120–122°; β -dibutylaminoethyl 2-furoate *hydrobromide*, m.p. 90.9–91.9°, and *benzoate hydrochloride*, m.p. 100.7–104.2°, and *hydrobromide*, m.p. 113.8–115.8°; γ -dibutylamino-*n*-propyl 2-furoate *hydrobromide*, m.p. 93.6–95.6°, and *benzoate hydrochloride*, m.p. 98.6–102.6°, and *hydro-*

bromide, m.p. 121.1—124.6°; β -phenylethylaminoethyl 2-furoate hydrobromide, m.p. 119.5—122.5°. The products have no or weak anaesthetic properties. M.p. are corr. R. S. C.

Bromination of 2-naphthyl benzoate. S. E. HAZLET (J. Amer. Chem. Soc., 1940, 62, 2156—2157).—2-C₁₀H₇·OBz with Br and a trace of Fe powder in AcOH gives 1-bromo-2-naphthyl benzoate, m.p. 98.5—99.5°, hydrolysed to and obtained from 1:2-C₁₀H₆Br·OH (acetate, m.p. 55—56°).

R. S. C.

Kolbe synthesis with alkyl-o-xenols. S. HARRIS and J. S. PIERCE (J. Amer. Chem. Soc., 1940, 62, 2223—2225).—By conversion of o-C₆H₄Ph·OH into the esters, Fries rearrangement (AlCl₃), reduction, and interaction with CO₂—K₂CO₃ at 110°, later 225°, are obtained 2-hydroxy-5-ethyl-, m.p. 161—164° (acetate, m.p. 156—160.5°), -5-n-propyl-, m.p. 137—143.5° (acetate, m.p. 148—151°), and -5-n-hexyl-diphenyl-3-carboxylic acid, m.p. 131—134°. o-Xenyl acetate, m.p. 63—63.5°, b.p. 139—141°/1 mm., propionate, b.p. 153—155°/2 mm., and n-hexoate, b.p. 174—177°/1.5 mm., 2-hydroxy-5-acetyl-, m.p. 167—168.5°, -5-propionyl-, m.p. 147.5—148°, and -5-n-hexoyl-diphenyl-, m.p. 86—88°, 2-hydroxy-5-ethyl-, b.p. 141—143°/1 mm., -5-n-propyl-, b.p. 150—152°/0.9 mm., and -5-n-hexyl-diphenyl-, b.p. 190—194°/2 mm., are described. Bactericidal properties are noted.

R. S. C.

Stereochemistry of diphenyls. L. Comparison of the interference of a methoxyl and hydroxyl group. R. ADAMS and H. M. TEETER (J. Amer. Chem. Soc., 1940, 62, 2188—2190; cf. A., 1939, II, 547).—1:2:5-C₆H₃MeBr·CN, m.p. 54—55°, b.p. 107—110°/3 mm., and H₂SO₄—HNO₃ at <15° give 6-bromo-5-nitro-m-toluenitrile (I), m.p. 100—103°, converted by NH₂Ac—NaOAc at 200° into 6-hydroxy-5-nitro-m-toluenitrile, m.p. 125—126°, which with boiling HCl—MeOH gives 5:1:6:3-NO₂·C₆H₂Me(OH)·CO₂Me, m.p. 102—103° (derived acid, m.p. 238—240°). Boiling 1:1 (vol.) H₂SO₄—H₂O hydrolyses (I) to 5:1:6:3-NO₂·C₆H₂MeBr·CO₂H, m.p. 212—213° (lit., 175—176°), the Me ester, m.p. 81—81.5°, of which with o-C₆H₄I·OMe and Cu-bronze at 240—250°, later 270°, gives 28% of 6-nitro-2'-methoxy-2-methyldiphenyl-4-carboxylic acid (II), m.p. 227—229°, converted by 40% HBr in AcOH into the 2'-OH-acid (III), m.p. 180—181° (brucine, softens at 169°, m.p. 205°, [α]_D²⁵ —22.4° in CHCl₃, and strychnine salt, m.p. 223—227°, [α]_D²⁵ —14.2° in CHCl₃). (II), but not (III), is resolved. Brucine and (II) in EtOH give only the brucine salt, +EtOH, m.p. 145—147°, [α]_D²⁵ —7.8° in CHCl₃, of the l-acid, m.p. 227—228°, [α]_D²⁵ —7.55° in AcOH, half-life 215 min. at 25°, ~11 min. in boiling AcOH; probably the l-base l-acid salt is stabilised by co-ordination with the solvent EtOH. The l-acid is also obtained by way of the strychnine, [α]_D²⁵ —13.4° in CHCl₃, and cinchonine, [α]_D²⁵ +140.0° in CHCl₃, salts. M.p. are corr. R. S. C.

Synthesis of hydroxymandelonitrile dibenzoates. K. E. HAMLIN, jun., and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1940, 29, 357—360).—BzCl (slight excess), C₅H₅N (1 mol.), and OH·C₆H₄·CHO (I) (1 mol.) yield o-(phenylhydrazone, m.p. 137—138°),

m-, m.p. 48.5—49°, and p-benzoyloxybenzaldehyde, m.p. 90—90.5° (lit. 72°; cf. Kopp, A., 1894, i, 128) (phenylhydrazone, m.p. 173—174°), which with saturated aq. NaCN and C₅H₅N followed by successive treatment with BzCl and dil. HCl afford o-, m.p. 92—92.5°, and m-hydroxymandelonitrile dibenzoate, m.p. 118.5—119.5°, and the p-isomeride, m.p. 144.5—145.5°, respectively. The latter are also obtained directly from (I), aq. NaCN (slight excess), and BzCl (2 equivs.) in C₅H₅N (2 equivs.). F. O. H.

5:8-Dibromo-2-naphthoic acid and 5:8-dibromo-2-naphthylamine. H. GOLDSTEIN and K. STERN (Helv. Chim. Acta, 1940, 23, 809—817; cf. A., 1938, II, 99).—5:8-Dibromo-2-naphthoic acid (I), m.p. 287° [Et ester (II), m.p. 94°], is obtained by the gradual addition of Br to β -C₁₀H₇·CO₂H (simplified prep. from β -C₁₀H₇·NH₂) in warm AcOH containing I and is purified through the Me ester, m.p. 152°. With PCl₅ or SOCl₂ it affords the chloride, m.p. 130°, which is transformed into the amide, m.p. 242°, and anilide, m.p. 217°. (II) and N₂H₄·H₂O in boiling EtOH afford 5:8-dibromo-2-naphthoylhydrazine (III), m.p. 231—235° [Ac derivative, m.p. 306° (decomp.)], which yields the corresponding hydrazones with COMe₂, PhCHO, and p-NO₂·C₆H₄·CHO, m.p. >180° after softening at 150°, 260°, and 275°, respectively. NaNO₂ and (III) in AcOH yield 5:8-dibromo-2-naphthazide (IV), m.p. ~112°, transformed by 50%, 70%, 80%, or 90% H₂SO₄ exclusively into (I). (IV) and the requisite boiling alcohol afford Me, m.p. 168—170°, and Et (V), m.p. 155°, 5:8-dibromo-2-naphthylcarbamate; (V) and boiling EtOH—conc. HCl give (I). In boiling glacial AcOH or in boiling C₆H₆ with subsequent exposure to moist air (IV) passes into s-di-5:8-dibromo-2-naphthylcarbamide, chars, without melting, at ~300°. With boiling C₆H₆ followed by NH₂Ph, (IV) gives N-phenyl-N'-5:8-dibromo-2-naphthylcarbamide, m.p. ~238° after shrinking at 228°. Successive treatments of carefully dried (IV) with boiling Ac₂O, H₂O, and EtOH—HCl lead to 5:8-dibromo-2-naphthylamine, m.p. 105° (yield 80—90%) [hydrochloride (VI); picrate, m.p. 221—228°; formyl, m.p. 226°, Ac, m.p. 215°, and Bz, m.p. 216°, derivatives], also obtained from (V) and boiling AcOH—H₂SO₄—H₂O. Diazotisation (iso-C₅H₁₁·O·NO) of (VI) in EtOH—conc. H₂SO₄ gives 1:4-C₁₀H₆Br₂. M.p. are corr. H. W.

5-Nitro-6-methyl-2-naphthoic acid. C. C. PRICE (J. Amer. Chem. Soc., 1940, 62, 2245).—2:6:1-C₁₀H₅Me₂·NO₂ and boiling HNO₃—H₂O give 5-nitro-6-methyl-2-naphthoic acid, m.p. 258—259°. 1:6:2-NO₂·C₁₀H₅Me·CO₂H has m.p. 238—239°.

R. S. C.

Constituents of natural phenolic resins. XVII. Synthesis of l-matairesinol. R. D. HAWORTH and F. H. SLINGER (J.C.S., 1940, 1098—1101; cf. A., 1939, II, 122).—O-Benzylvanillin, (CH₂·CO₂Et)₂, and NaOEt in Et₂O afford a non-cryst. product, reduced (Na—Hg, H₂O, CO₂) to meso- α - β -di-(4-benzoyloxy-3-methoxybenzyl)succinic acid (I), m.p. 203° (pyrolysis at 220° or AcCl does not give the anhydride), converted by Ac₂O into a product, m.p. 90—110°, or by P₂O₅—C₆H₆ into a substance, m.p. 148°, hydrolysed by alkali to a substance, m.p. 129—130°. (I) and boiling

conc. HCl-AcOH afford meso- $\alpha\beta$ -di-(4-hydroxy-3-methoxybenzyl)succinic acid (II), m.p. 228—229°; MeOH-HCl then gives the *Me* ester, m.p. 169—170°, but Me_2SO_4 -aq. NaOH gives meso- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic acid and its *Me* ester (cf. A., 1939, II, 476). (II) and Ac_2O afford an oil [probably *trans*- $\alpha\beta$ -di-(4-acetoxy-3-methoxybenzyl)succinic anhydride], which with boiling H_2O gives dl- $\alpha\beta$ -di-(4-acetoxy-, m.p. 129—130°, or with N-HCl affords dl- $\alpha\beta$ -di-(4-hydroxy-3-methoxybenzyl)succinic acid (III), m.p. 194—195°. (III) and strychnine in CHCl_3 give the strychnine salt (IV), $+9\text{H}_2\text{O}$, shrinks at 145°, m.p. 247°, $[\alpha]_D^{25} -18^\circ$ in CHCl_3 , and thence (NaHCO_3) the l-acid (V), m.p. 109°, $[\alpha]_D^{25} -47^\circ$ in EtOH. The acid recovered (NaHCO_3) from the mother-liquors from (IV) gives a brucine salt, $[\alpha]_D^{25} -54^\circ$ in CHCl_3 , and thence the d-acid, m.p. 106—108°, $[\alpha]_D^{25} +40^\circ$ in EtOH. (V) and Ac_2O afford a gum, converted by Al-Hg in C_6H_6 - Et_2O - H_2O at room temp. into an oil, which with KOH-MeOH, followed by aq. HCl at 100°, gives l-matairesinol, m.p. 116—117°, $[\alpha]_D^{25} -46^\circ$ in COMe_2 , identical with that from *Podocarpus spicatus*. Its di-*p*-nitrobenzoate, m.p. 95—156° (MeOH- CHCl_3 ; solvated) or 157—158° (from aq. AcOH), $[\alpha]_D^{25} +9^\circ$ in CHCl_3 , is also obtainable from natural l-matairesinol. The d- and dl-forms obtained similarly are not pure, but yield the respective Me_2 ethers with Me_2SO_4 -aq. NaOH. A. T. P.

Constituents of natural phenolic resins. XVIII.
1:2:3:4-Tetrahydronaphthalene-2:3-dicarboxylic acid and the 1-phenyl derivative. R. D. HAWORTH and F. H. SLINGER (J.C.S., 1940, 1321—1327).—Reduction (Na-Hg in hot aq. NaOH) of 2:3- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ gives acids converted by AcCl into a mixture of *cis*-(I), m.p. 183° (identical with that of Perkin *et al.*, J.C.S., 1888, 53, 12), and *trans*-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride (II), m.p. 225—226°. Hydrolysis of (I) and (II) gives respectively the *cis*-, m.p. 195° (*loc. cit.*), and *trans*-acid, m.p. 226—227°; the latter is resolved by strychnine into the d-, $[\alpha]_D^{25} +85.5^\circ$, and l-*trans*-acids, m.p. 182—183°, $[\alpha]_D^{25} -35^\circ$ in CHCl_3 (strychnine salts, m.p. 195—240° and 170—180°, respectively). Dehydration (Ac_2O) of the mixed *cis*- and *trans*-acids yields only (I), also produced by boiling (II) with Ac_2O for 15 min. Esterification (Fischer-Speier or Ag salt method) of the *cis*- and *trans*-acids yields *Me* esters, m.p. 68—68.5° and 44.5—45°, respectively. The former ester with EtOH- NaOEt gives the latter. Reduction (Al-Hg) of (I) and (II) yields the *cis*- and *trans*-lactones, m.p. 133—134° and 156°, respectively, of 2-hydroxymethyl-1:2:3:4-tetrahydronaphthalene-3-carboxylic acid, hydrolysis (MeOH-NaOH) and acidification of which gives the original lactones without change of configuration. Mixed 1-phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acids, m.p. 170—180° (A., 1939, II, 476) [form, m.p. 218—219° (decomp.), isolable], with AcCl give a mixture of 1-phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydrides, A, m.p. 240—241°, B, m.p. 155—156°, C, m.p. 171—172°, and D, m.p. (crude) 193—199°. Cautious hydrolysis of anhydrides A, B, and C gives the acids, A, m.p. 236—237°, B, m.p. 218—219° (cf. above), and C, m.p. 162—163°,

converted by CH_3N_3 into the Me_2 esters, A, m.p. 108—109°, B, m.p. 102—103°, and C, m.p. 113—114°, or by AcCl into the original anhydrides. The crude anhydride D with CH_3N_3 gives Me_2 esters B (80%) and D (20%), m.p. 127°. With boiling Ac_2O , anhydrides B and C are unaffected, but A and D yield anhydrides C and B, respectively. With MeOH-HCl acids A and C yield the corresponding Me_2 esters, but B gives a mixture of esters B and D. All four esters with NaOH or NaOEt yield acid A. It is concluded that the configurations of the acids are: A *trans*(1:2)-*trans*(2:3)-, B *cis*(1:2)*cis*(2:3)-, C *trans*(1:2)*cis*(2:3)-, D (unstable) *cis*(1:2)*trans*(2:3)-. The relative stabilities of these configurations are discussed. Anhydrides A, B, and C are sulphonated by cold conc. H_2SO_4 , but with AlCl_3 in PhNO_2 yield 3:4-benzo-1:2:10:11-tetrahydrofluorene-1-carboxylic acids, A [*trans*(10:11)*trans*(1:10)], m.p. 203—204°, B [*cis*(10:11)*cis*(1:10)], m.p. 220—221°, and C [*trans*(10:11)*cis*(1:10)], m.p. 163—164°, respectively. All of these with Se yield 3:4-benzfluorenone. On decarboxylation A and C yield *trans*(10:11)-3:4-benzo-1:2:10:11-tetrahydrofluorenone, m.p. 161—163°, whilst B gives the *cis*(10:11)-form, m.p. 131—134°. From these results it is suggested that naturally occurring 1-phenylnaphthalene-lignans have the stable *trans*(1:2)*trans*(2:3)-structure. A. Li.

Behaviour of oximino- and isonitro-compounds under the conditions of Van Slyke's determination of amino-nitrogen. M. SCHENCK and J. RESCHKE (Ber., 1940, 73, [B], 200—205).—The behaviour of acet- (I) and benz-hydroxamic acid (II), and of the diketo- (III), oximino-keto- (IV) and -lactam- (V), and nitro-keto- (VI), -oximino- (VII), and -lactam-hydroxamic acid (VIII) from cholic acid, deoxybiliaric acid oxime (IX), and dehydrocholic acid trioxime (X) in Van Slyke's apparatus is studied. Except for (I), and $\text{NH}_2\text{OH}\cdot\text{HCl}$, both of which give some N_2O , the gas is largely N_2 : (II) gives 19%, (III) 17%, (IV) 114%, (V) 128%, (VI) 6—9%, (VII) 19%, (VIII) 12%, (IX) 23%, and (X) 117% of the theoretical for evolution of 1N_2 per mol. of hydroxamic acid. This shows the strong influence of position and substitution on evolution of N_2 , which seems particularly favoured by N-OH at C_{17} . Possible explanations of the results are discussed. E. W. W.

Effect of substitution on thermal decomposition of gaseous benzaldehyde.—See A., 1940, I, 414.

Decomposition of benzylidene diacetate, o-chlorobenzylidene diacetate, and benzylidene dibutyrate.—See A., 1940, I, 414.

Schiff bases from p-aminothymol. W. T. SUMERFORD, W. H. HARTUNG, and G. L. JENKINS (J. Amer. Chem. Soc., 1940, 62, 2082—2083).—4-Benzylidene-, m.p. 149°, 4-2'-hydroxy- (I), m.p. 170°, 4-2'-hydroxy-4'-methyl-, m.p. 155°, 4-4'-methoxy- (II), m.p. 160°, 4-4'-hydroxy-3'-methoxy-, m.p. 194°, and 4-3':4'-methylenedioxy-benzylidene-, m.p. 161—162°, and 4-cinnamylidene-aminothymol ($\text{OH} = 1$), m.p. 154°, are prepared. (I) and (II) are antipyretic for cats. (I) is not toxic. M.p. are corr. R. S. C.

Reaction of aldoximes with diazomethane. A. F. THOMPSON, jun., and M. BAER (J. Amer. Chem. Soc., 1940, **62**, 2094—2096).—Contrary to Forster *et al.* (J.C.S., 1909, **95**, 425), the appropriate $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ with CH_2N_2 in Et_2O gives α -*o*-, m.p. 59°, α -*m*-, m.p. 61°, β -*m*-, m.p. 72°, and α -*p*- (I), m.p. 101·5°, -nitrobenzaldoxime *O*-Me ether together with small amounts of the α -*o*- [hydrochloride, m.p. 128—132° (lit., 125—134°)], α -*m*-, m.p. 117°, β -*m*-, m.p. 86—88°, α -*p*- (II), m.p. 201° (lit., 205°), and β -*p*- (III), m.p. 147—149°, -nitrobenzaldoxime *N*-Me ether. The β -*p*-aldoxime *O*-Me ether was not obtained. The structure of the *N*-Me ethers is proved by ready acid hydrolysis to the aldehyde and $\text{NHMe}\cdot\text{OH}$ and by conversion of (III) into (II) when melted. CH_2N_2 has no effect on (I). Only (I) is formed from the oxime, KOH, and MeI in Et_2O . R. S. C.

Kinetic study of the reaction of acetophenone with benzaldehyde.—See A., 1940, I, 414.

Addition of β -unsaturated alcohols to the active methylene group. II. Action of ethyl acetoacetate on cinnamyl alcohol and phenylvinylcarbinol. M. F. CARROLL (J.C.S., 1940, 1266—1268; cf. A., 1940, II, 266).— $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (convenient prep.) and $\text{KOAc}\cdot\text{AcOH}$ at 90—100° give mixed acetates, hydrolysed by 40% aq. $\text{NaOH}\cdot\text{EtOH}$ to $\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}\cdot\text{OH}$ (I) and $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ (II). $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, (II), and NaOAc at 165°, then at 185—240°, afford γ -phenyl- Δ^4 -hexen- ϵ -one (III) and cinnamyl acetoacetate and acetate. (I) similarly (220°; KOAc) yields cinnamylacetone; no transposition occurs. (III) and KMnO_4 -aq. NaOH give α -phenyl-lævulic acid, also obtained from $\text{CHBrPh}\cdot\text{CO}_2\text{Et}\cdot\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}\cdot\text{K}_2\text{CO}_3\cdot\text{COMe}_2$.

A. T. P.

Substances with odour of violets. VIII. Synthesis of 1 : 1 : 6-trimethyl-3- γ -keto- Δ^4 -butenylcycloheptene. M. STOLL and W. SCHERRER (Helv. Chim. Acta, 1940, **23**, 941—948; cf. Barbier, A., 1940, II, 217).—Addition of dihydroisophorone (I) followed by LiCl in MeOH to CH_2N_2 in Et_2O gives a mixture of ketones which is partly purified through the semicarbazones, which are hydrolysed and treated with conc. aq. NaHSO_4 , whereby 3 : 3 : 5-trimethylcycloheptanone (II), b.p. 87—88°/12·5 mm. (semicarbazone, m.p. 192—193°), remains unattacked (yield 21%). The NaHSO_4 compound yields 3 : 5 : 5-trimethylcycloheptanone, b.p. 86—88°/12 mm. (yield 12%) [semicarbazone, m.p. 196—197° (varies with rate of heating); picrate, m.p. 214—215°, of compound with aminoguanidine; *p*-nitrophenylhydrazine, m.p. 154—155°]. A third product of the change

is the oxide, $\text{CH}_2\cdot\text{C}(\text{CHMe})_2\cdot\text{CH}_2\cdot\text{C}(\text{CHMe})_2\cdot\text{CH}_2$, b.p. 67—69°/13 mm. (yield 46%). (II) is converted by NaOEt and isoamyl formate into 3 : 3 : 5-trimethyl-7-hydroxymethylenecycloheptanone, b.p. 108—110°/10 mm., oxidised (KMnO_4 in alkaline solution) to $\beta\beta\delta$ -trimethylpimelic acid, the Th salt of which at 320—350° passes into (I). Anhyd. HCN and a little KCN transform (II) into the cyanohydrin, b.p. 103°/0·2 mm. (corresponding amide, m.p. 131°), hydrolysed and esterified to *Me* 1-hydroxy-3 : 3 : 5-trimethylcycloheptane-1-carboxylate, b.p. 123—128°/14 mm., which

is converted by SOCl_2 followed by BaCl_2 at 250°/0·8 mm. into *Me* 3 : 3 : 5-trimethyl- Δ^1 -cycloheptenecarboxylate, b.p. 118—122°/18 mm. This is hydrolysed to solid, m.p. 116—117° (chloride, b.p. 130—131°/18 mm.), and liquid acids (chloride, b.p. 123—129°/15 mm.). The two chlorides are catalytically reduced (Fröschl) to 3 : 3 : 5-trimethyl- Δ^1 -cycloheptenaldehyde (III) (semicarbazone, m.p. 172—174°) and the corresponding saturated alcohol, b.p. 122—126°/16 mm. COMe_2 and (III) condense to 1 : 1 : 6-trimethyl-3- γ -keto- Δ^4 -butenylcycloheptene, b.p. 157—160°/17 mm. (semicarbazone, m.p. 208—209°), which does not resemble irone in odour. The cycloheptane ring is not sufficient in itself to give the irone perfume.

H. W.

Substances with odour of violets. IX. Synthesis of nuclear-methylated homologues of ionone, 1 : 1 : 3 : 6-tetramethyl-2- γ -keto- Δ^4 -butenylcyclohexene. L. RUZICKA and H. SCHINZ (Helv. Chim. Acta, 1940, **23**, 959—974).—Methylheptenone (I), purified through the semicarbazone, is condensed with Zn and $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 to the OH-ester, b.p. 130—132°/12 mm., which is smoothly dehydrated by $\text{PBr}_3\cdot\text{C}_5\text{H}_5\text{N}$ but not by AcOH and fused ZnCl_2 to nearly homogeneous Et geranate (II), hydrolysed to geranic acid (III), b.p. 111—112°/0·25 mm. (I) purified through its NaHSO_3 derivative is converted by similar treatment into (II) accompanied by a considerable proportion of Et cyclogeranate (IV), b.p. 100—101°/12 mm., separated from (II) by using its more difficult hydrolysis. (III) is transformed by SOCl_2 into the chloride, b.p. 95—105°/0·6 mm., and thence the anilide, b.p. 180°/0·2 mm. This is converted by PCl_5 in C_6H_6 into the imino-chloride, which gives citral in very poor yield when acted on by CrCl_2 . (III) is not successfully cyclised by H_2SO_4 or H_3PO_4 but is readily converted by HCO_2H at 100° into α -cyclogeranic acid (V), m.p. 104—106° after softening at 97°, identical with that obtained by treating (IV) with $\text{KOH}\cdot\text{MeOH}$ at 150—170°. (V) is readily converted (Merling's method, A., 1908, i, 653) through the chloride, b.p. 87—88°/12 mm., and *o*-toluidide, m.p. 150°, into citral. The prep. of β -dimethyl- Δ^8 -hepten- ζ -one (VI), b.p. 76°/13 mm. (semicarbazone, m.p. 161—163°), from $(\text{CH}_2\cdot\text{CMe})_2$ is described. The Reformatsky condensation of (VI) leads to the OH-ester, b.p. 139—143°/12 mm., transformed by PBr_3 and $\text{C}_5\text{H}_5\text{N}$ in light petroleum followed by distillation into Et methylgeranate, b.p. 116—121°/12 mm., hydrolysed by $\text{KOH}\cdot\text{EtOH}$ at 100° to methylgeranic acid (VII), b.p. 122—125°/0·35 mm., with about 25% of Et methylcyclogeranate, b.p. 105—108°/12 mm., hydrolysed ($\text{KOH}\cdot\text{EtOH}$ at 160—170°) to methylcyclogeranic acid (VIII), m.p. 65—70°. The cyclisation of (VII) to (VIII) by 100% HCO_2H at 100° is described. (VIII) is transformed by SOCl_2 in light petroleum into the chloride, b.p. 100—102°/14 mm., which gives the *o*-toluidide (IX), m.p. 156—157°, and the anilide (X), m.p. 131—132°. (IX) and (X) are reduced (Merling) to a mixture of at least two methylcyclocitrals, b.p. 94—97°/12 mm. (semicarbazones, m.p. 214—215° and 140—145°), which are condensed with COMe_2 to 1 : 1 : 3 : 6-tetramethyl-2- γ -keto- Δ^4 -butenyl- Δ^2 - or - Δ^3 -cyclohexene (XI), b.p. 105—108°/0·75 mm., which is allied by its odour

to the ionones but not to irone. (XI) gives a non-cryst. *p*-bromophenylhydrazone and a *phenylsemicarbazone* (divisible into fractions, m.p. 130—135° to 165—166°). (XI) is hydrogenated (H_2 -Pd-EtOAc) to the H_4 -ketone [*semicarbazone*, m.p. 183—186° (not const.)]. H. W.

***p*-Phenylphenacyl esters.** H. E. CARTER (J. Amer. Chem. Soc., 1940, 62, 2244—2245).—*p*-Phenylphenacyl β -phenylisobutyrate, m.p. 71—72°, γ -phenyl- α -methyl-*n*-butyrate, m.p. 62—63°, and δ -phenyl- β -methyl-*n*-valerate, m.p. 66—67°, are prepared.

R. S. C.

Trimerisation of mesityl vinyl ketone. R. C. FUSON and C. H. MCKEEVER (J. Amer. Chem. Soc., 1940, 62, 2088—2091).— $AlCl_3$ added to $Cl \cdot [CH_2]_2 \cdot COCl$ and s - $C_6H_3Me_3$ in CS_2 at 10° gives *mesityl vinyl ketone* (I) (63%), b.p. 99—101°/3.5 mm.; under other conditions at room temp. 25% of (I) and (?) β -*mesitylpropionomesitylene*, m.p. 80—81°, are obtained. Hydrogenation (Raney Ni; room temp./2 atm.; EtOH) of (I) gives 1 : 3 : 5 : 2- $C_6H_2Me_3 \cdot COEt$ [$(NO_2)_2$ -derivative, m.p. 143.5—144.5°]. With Br, (I) gives $\alpha\beta$ -*dibromopropionomesitylene*, m.p. 78.5—79.5°, reconverted into (I) by NaI. $MgMeI$ converts (I) into 1 : 3 : 5 : 2- $C_6H_2Me_3 \cdot COPr^a$, b.p. 120—121°/7 mm. [$(NO_2)_2$ -derivative, m.p. 133—135°], also obtained by the Friedel-Crafts reaction. HCl adds to (I) giving β -*chloropropionomesitylene*, m.p. 46—47.5°. (I) is stable to heat alone or with Bz_2O_2 or ascaridole, but with K_2CO_3 in boiling MeOH gives 65—70% of 1 : 3 : 5-*trimesitylcyclohexane* (II), m.p. 210—212°, with some *dimeride*, m.p. 83—83.5°, and also a *trimeride* [? stereoisomeride of (II)], m.p. 150—151°. 1 : 3 : 5- $C_6H_3(CO_2Me)_3$ (from the acid and H_2SO_4 -MeOH) with H_2 -Raney Ni in dioxan at 175°/2750 lb. gives stereoisomeric H_6 -esters, b.p. 163—164°/2.5 mm. (yields a form, m.p. 42—44°). Hydrolysis by boiling 15% NaOH, interaction with $SOCl_2$, and then s - $C_6H_3Me_3 \cdot AlCl_3 \cdot CS_2$ gives (II). R. S. C.

Synthesis of baeckeol. B. A. HEMS and A. R. TODD (J.C.S., 1940, 1208—1209).—Phlorisobutyrophenone and $MeI \cdot COMe_2 \cdot K_2CO_3$ afford 2-hydroxy-4 : 6-dimethoxy-3-methylisobutyrophenone, m.p. 103—104° [acetate, two forms, m.p. 73° (prisms from aq. MeOH at low temp.) and 79—80° (needles from hot aq. MeOH or from other form at 75°)], identical with baeckeol (cf. Ramage *et al.*, A., 1940, II, 223).

A. T. P.

Phenanthrene derivatives. X. Acetylation of 4-methylphenanthrene. W. E. BACHMANN and R. O. EDGERTON (J. Amer. Chem. Soc., 1940, 62, 2219—2223; cf. A., 1938, II, 184).— $C_{10}H_7 \cdot [CH_2]_3 \cdot COCl$ and $SnCl_4$ in C_6H_6 give 4-keto- (88%), m.p. 69—70°, converted by $MgMeI$ into 4-hydroxy-4-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (80%), m.p. 109—110°, which with $Pd-C$ at 310—320° gives 4-methylphenanthrene (I) (85%), m.p. 49—50°. With $AcCl$ and $AlCl_3$ in $PhNO_2$ at -10° this gives 1-acetyl-4- (II) (50%), m.p. 84—85° and 71—72.5° (picrate, m.p. 142—143°), and 3-acetyl-5-methylphenanthrene (III) (15%), m.p. 98—99° (picrate, m.p. 107—110°). Structures are proved as follows. α -1-Naphthylethyl bromide (prep. from the carbinol by PBr_3 in Et_2O at -10°), unstable, m.p. 37—40°, with

$CHNa(CO_2Et)_2$ in EtOH gives an ester, whence by hydrolysis and heating at 160—180° 1- $C_{10}H_7 \cdot CHMe \cdot CH_2 \cdot CO_2H$ (90%), m.p. 108—110°, is obtained. The Arndt-Eistert procedure then yields γ -1-naphthylvaleric acid (68%), m.p. 78—80°, the chloride of which is cyclised ($SnCl_4 \cdot C_6H_6$) to 1-keto-4-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (IV) (91%), m.p. 81.5—83°. $MgMeI$ converts (IV) into a carbinol, which with $Pd-C$ at 300—320° gives 1 : 4-dimethylphenanthrene, m.p. 50—51.5° (lit., 50—51°, 77°) [picrate, m.p. 143—143.5° (lit., 143.5°, 155°)]. $Zn-Hg-HCl-AcOH-PhMe$ and dehydrogenation convert (IV) into (I). The product from (IV) and $MgEtBr-Et_2O$ treated with $Pd-C$ at 300—320° gives 4-methyl-1-ethylphenanthrene, an oil (picrate, m.p. 104—106°), obtained also by Clemmensen reduction of (II). $PhEt$, $(CH_2 \cdot CO)_2O$, and $AlCl_3$ at <0° and then at room temp. give *p*- $C_6H_4Et \cdot CO \cdot [CH_2]_2 \cdot CO_2H$ (57%), new m.p. 107—109°, reduced (Martin-Clemmensen) to *p*- $C_6H_4Et \cdot [CH_2]_3 \cdot CO_2H$, new m.p. 72.5—74°, which yields $(SOCl_2 \cdot C_5H_5N)$; then $AlCl_3-CS_2$ at <0° 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (87%), b.p. 108—110°/0.6 mm. With $NaOMe$ and $Me_2C_2O_4$ in $C_6H_6-N_2$ this gives *Me* 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylglyoxylate (82%), m.p. 35.5—37°, which with powdered soft glass at 190—200° gives CO and *Me* 1-keto-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (85%), b.p. 168—170°/1.5 mm. Condensation with $Na-Br[CH_2]_3 \cdot CO_2Me \cdot C_6H_6$ and later hydrolysis by conc. $HCl-AcOH$ gives γ -1-keto-7-ethyl- (68%), m.p. 74—75.5°, reduced (Martin-Clemmensen) to γ -7-ethyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylbutyric acid (V), m.p. 108.5—110°. The *Me* ester (prep. by CH_2N_2) of (V) is dehydrogenated by $Pd-C$ at 235—255° and then hydrolysed to γ -7-ethyl-2-naphthylbutyric acid (90%), m.p. 105.5—106.5°. Conversion thereof by PCl_5 in C_6H_6 into the chloride and cyclisation ($SnCl_4$) gives 4-keto-6-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (80%), m.p. 52.5—53.5°, whence $MgMeI$ and later $Pd-C$ yields 5-methyl-3-ethylphenanthrene [picrate, new m.p. 113.5—115°; s - $C_6H_3(NO_2)_3$, new m.p. 127—128°, and 1 : 2 : 4 : 6- $C_6H_2Me(NO_2)_3$ compound, m.p. 78—79.5°], also obtained by reduction of (III). R. S. C.

Biochemistry of filamentous fungi. VI. Mycelial constituents of *Oospora sulphureo-ochracea*. Trimethylsulochrin and its fission products. H. NISHIKAWA (Bull. Agric. Chem. Soc. Japan, 1940, 16, 97—99; cf. A., 1940, II, 92).—Repeated methylation (Me_2SO_4) of sulochrin [*Me* 2 : 6 : 4'-trihydroxy-6'-methoxy-4-methylbenzophenone-2'-carboxylate] yields trimethylsulochrin (I), m.p. 157°, which with conc. H_2SO_4 at 100° (bath) gives dimethyl-*p*-orsellinic acid and *Me* dimethyl- α -resorcylic acid. Hydrolysis ($KOH-MeOH$) of (I) yields 2 : 6 : 4' : 6'-tetramethoxy-4-methylbenzophenone-2'-carboxylic acid, m.p. 194°.

J. N. A.

Lignin and related compounds. XLVIII. Identification of vanillin and vanilloyl methyl ketone as ethanolysis products from spruce wood. L. BRICKMAN, W. L. HAWKINS, and H. HIBBERT (J. Amer. Chem. Soc., 1940, 62, 2149—2154; cf. A., 1940, II, 254).—Separation of vanillin and vanilloyl *Me* ketone [4-hydroxy-3-methoxyphenyl

Me diketone] (I) from the ethanolysis products from spruce wood by methods involving distillation and fractionation of 2:4-dinitrophenylhydrazones is detailed. (I), m.p. 72–73°, b.p. 125°/0.2 mm., gives a *quinoxaline* derivative, m.p. 162–163°, *mono*-, m.p. 215–216°, and *di-semicarbazone*, m.p. 241°, and 2:4-dinitrophenylhydrazone, m.p. 226–227° (*Me ether*, m.p. 194–195°). 3:4:1-(OMe)₂C₆H₃·COMe, HCO₂Et, and Na wire in C₆H₆ give *veratroyl acetaldehyde*, an oil (Na salt; 2:4-dinitrophenylhydrazone, m.p. 189–190°). Addition of 3:4:1-OMe·C₆H₃(OH)·CO·CHMe·OH to CuSO₄ in aq. C₅H₅N at 100° gives (I), but other methods of synthesis failed. (I) may form one member of an oxidation-reduction system functioning in plant respiration.

R. S. C.

Preparation of 4:4'-dicyanodiphenyl and diphenyl diketones. (MISSES) C. DE MILT and M. SARTOR (J. Amer. Chem. Soc., 1940, 62, 1954–1955). —(p-CN·C₆H₄)₂ [obtained in 66% yield from neutralisation (p-N₂Cl·C₆H₄)₂ (1 mol.), NiCl₂ (1 mol.), and KCN (4 mols.)] with MgRCl gives ketimine hydrochlorides, hydrolysed by boiling, very dil. AcOH to 4:4'-dibenzoyl-, m.p. 218° (*dioxime*, m.p. 247°), -*di*(phenylacetyl)-, m.p. 208–210° (*dioxime* m.p. 202–205°), and -*dipropionyl-diphenyl*, m.p. 163–165° (*dioxime*, m.p. 226–229°).

R. S. C.

Substances with odour of violets. VII. Synthetic problems in the irone series. Synthesis of 3:5:5-trimethylcycloheptanone. L. RUZICKA, H. SCHINZ, and C. F. SEIDEL (Helv. Chim. Acta, 1940, 23, 935–941; cf. A., 1935, 672).—Addition of dihydroisophorone and isoamyl formate to NaOEt under Et₂O yields hydroxymethylenedihydroisophorone, b.p. 99–101°/13 mm., converted by successive oxidation with KMnO₄-NaOH, esterification with conc. H₂SO₄ and MeOH, and reduction by Na in abs. EtOH into βδδ-trimethylhexane-α,ε-diol, b.p. 150°/12 mm. This is converted by HBr at 120–130° into the corresponding dibromide, b.p. 135°/12 mm., which gives the *dinitrile*, b.p. 144–145°/0.3 mm. The dry Th salt of the dicarboxylic acid when distilled in a vac. yields 3:5:5-trimethylcycloheptanone, b.p. 87°/11 mm. (*semicarbazone*, m.p. 187–189°; *p*-nitrophenylhydrazone, m.p. 153–154°; *picrate*, m.p. 212–213°, of the aminoguanidine compound).

H. W.

[Attempted] synthesis of Wieland's C₁₃H₂₀O₆ acid from bile acids. S. K. RANGANATHAN (Current Sci., 1940, 9, 276–277; cf. Wieland *et al.*, A., 1933, 609; Baker *et al.*, *ibid.*, 935).—Et aconitate, CH₂(CO₂Et)₂, and a trace of EtOH-free NaOEt (no solvent) give Et *n*-butane-αβγδ-pentacarboxylate, b.p. 195°/3 mm., hydrolysis and decarboxylation of which affords *meso*-, (I), m.p. 189°, and *dl*-, m.p. 236°, -butane-αβγδ-tetracarboxylic acid. The Et ester, b.p. 180°/2 mm., of (I) is cyclised to Et₃ cyclopentanone-2:3:4-tricarboxylate, b.p. 171°/2 mm. (hydrolysed to cyclopentanone-3:4-dicarboxylic acid), the K derivative of which with CHMeBr[CH₂]₂·CO₂Et (excess) yields Et γ-2-keto-1:4:5-tricarbethoxy-cyclopentylvalerate (II), b.p. 218°/2 mm. Attempted hydrolysis, with or without decarboxylation, of (II) was unsuccessful. Et β-methylbutane-αβγδ-penta-

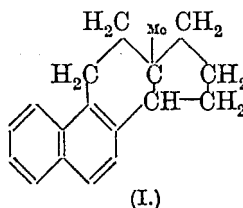
carboxylate, b.p. 207°/3 mm., affords β-methylbutane-αβγδ-tetracarboxylic acid, m.p. 193° (anhydride, m.p. 187°), the Et ester, b.p. 186°/2 mm., of which is cyclised to Et₃ 3-methylcyclopentanone-2:3:4-tricarboxylate, b.p. 176–178°/2 mm.

A. Lr.

Asymmetry of the aliphatic nitro-group. Resolution of 9-nitro-2-benzoylfluorene. F. E. RAY and S. PALINCHAK (J. Amer. Chem. Soc., 1940, 62, 2109–2113).—The *aci*-form (I) of 9-nitro-2-benzoylfluorene is resolvable only when the lone pair of electrons on C₉ is co-ordinated with a solvent mol. The K salt, prepared (83–88%) from 2-benzoylfluorene, KOEt, and EtNO₃ in EtOH-Et₂O, is stable when dry, but in solution gives 2-benzoylfluorenone (II) and HNO₂, and with aq. acid gives (I), yellow, m.p. 80–84° (decomp.). In boiling EtOH (I) gives a red dimeride, 9:9'-*dinitro*-2:2'-*dibenzoyl*-9:9'-*di*fluorenyl (III), m.p. 135–137°. The menthyl ester of (I) is obtained as an oil, [α]_D²⁵ –218° in EtOH, containing EtOH, removal of which causes decomp. to menthol, (II), and (III). The K salt gives the *brucine* salt, + EtOH (IV), sinters at 160°, m.p. 175–185° (decomp.). When this is treated with KOH-EtOH, the freshly prepared mixture has [α]_D –65°, changing in 30 hr. to the [α]_D of *brucine*; the difference (18°) is the approx. [α]_D of the ion of (I). When aq. KOH is used, racemisation occurs at once and there is no change in α. When KOAc-EtOH is added to (IV), there is an immediate change in [α], probably due to replacement of the co-ordinated EtOH by KOAc; later the inactive K salt is pptd. Dil. HCl at –10° ppts. inactive (I) from (IV), but in AcOH (IV) gives [α]_D +5.54° → –4.04° in 0.5 hr.; probably active (I) exists temporarily, co-ordinated with AcOH. With Br-CHCl₃, (IV) gives an active bromide, which rapidly racemises and decomposes. Kinetic studies show that racemisation and decomp. of (IV) occur simultaneously in CHCl₃ or BuOH (co-ordinates), but in C₅H₅N racemisation at first occurs alone. 9-Nitro-2:7-dibenzoylfluorene (V), m.p. 194–195°, gives a K salt, solvent-free and + BuOH, and thence a *brucine* salt, [α] +67° in CHCl₃, +78° in C₅H₅N, unchanged for 2 hr. (later decomp.), the symmetry of (V) accounting for absence of resolution. Prep. (Friedel-Crafts) of (V) gives also some (?) 2:3-dibenzoylfluorene, m.p. 119–120°.

R. S. C.

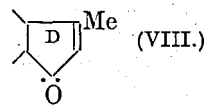
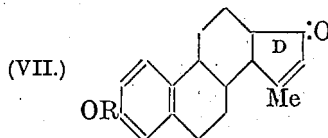
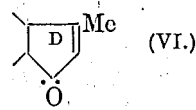
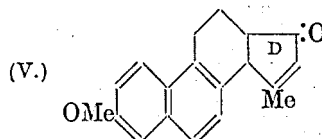
Synthesis of *cis*- and *trans*-17-equilenone. W. E. BACHMANN and A. L. WILDS (J. Amer. Chem. Soc., 1940, 62, 2084–2088; cf. A., 1940, II, 225).—Equilenin derivatives are named on the basis of equilenane for (I). 1-Keto-1:2:3:4-tetrahydrophenanthrene (improved prep.), Me₂C₂O₄, and NaOMe in C₆H₆-N₂ give *Me* 1-keto-1:2:3:4-tetrahydrophenanthrene-2-glyoxylate, ? dimorphic, m.p. 90–91° and 106–108°, which in presence of powdered glass at 180–200° gives *Me* 1-keto-1:2:3:4-tetrahydrophenanthrene-2-carboxylate, m.p. 88–90° after softening. With MeOH-NaOMe and MeI in boiling C₆H₆ this gives *Me* 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene-



2-carboxylate (I), m.p. 79.5—80.5°, which by the Reformatsky reaction gives *Me*₂ 1-hydroxy-2-methyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylate-1-acetate, m.p. 131—133° (with 40% KOH gives 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene). Dehydration then yields anti-2-carboxy-2-methyl-1:2:3:4-tetrahydro-1-phenanthrylideneacetic acid (II), m.p. 220—221° [*Me*₂ ester (III), m.p. 110—111°], and the anhydride, m.p. 188.5—189.5°, of the syn-acid. Boiling NaOH-MeOH-H₂O converts (III) into the 2-*Me*₁ ester, m.p. 197—199°, which with KMnO₄-H₂O-C₆H₆ at 0° gives (I), thus proving that the *Me* has not migrated. 2% Na-Hg in H₂O reduces the K salt of (II) to 2-methyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylic-1-acetic acid, stereoisomeric α-, m.p. 228—229° [*Me*₂ ester (IV), m.p. 106—107°], and β-form (V), m.p. (+ solvent) 160—165° (gas), (anhyd.) 182—183°. With NaOH-MeOH-H₂O, (IV) gives the 2-*Me*₁ α-ester, m.p. 133—134°, which yields (Arndt-Eistert) *Me* α-2-carbomethoxy-2-methyl-1:2:3:4-tetrahydrophenanthrene-1-propionate, m.p. 98—99° [derived dicarboxylic acid (VI), m.p. 213—213.5°], cyclised by NaOMe-C₆H₆-N₂ to *Me* α-dl-17-equilenone-16-carboxylate, m.p. 124—125°, sublimes at 200°/0.4 mm. Boiling conc. HCl-AcOH-H₂O-N₂ then gives α-dl-17-equilenone (VII), m.p. 100—101° (picrate, m.p. 109.5—110.5°), obtained also less well from (VI) by Ac₂O or by pyrolysis of the Pb salt, and converted by reduction and dehydrogenation into 1:2-cyclopentenophenanthrene. Similarly, (V) yields the 2-*Me*₁ ester, m.p. 156—158°, *Me* β-dl-17-equilenone-16-carboxylate, m.p. 134—134.5° (vac.), and β-dl-17-equilenone (VIII), m.p. 188.5—189.5° (vac.). (VII) and (VIII) do not induce oestrus in 0.5-mg. doses. R. S. C.

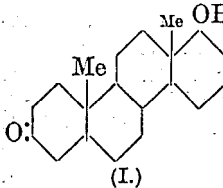
Steroids and sex hormones. LXIII. Attempted synthesis of oestrogens with use of αβ-diacylethylene. M. W. GOLDBERG and P. MÜLLER (Helv. Chim. Acta, 1940, 23, 831—840).—Contrary to Dane *et al.* (A., 1937, II, 500), 1-acetylenyl-1:2:3:4-tetrahydro-1-naphthol (I), b.p. 104°/0.2 mm., is the sole product of the action of CH₃C≡CMgBr (II) on 1-keto-1:2:3:4-tetrahydronaphthalene. Partial reduction (H₂-Pd-CaCO₃-EtOH) of it gives 1-vinyl-1:2:3:4-tetrahydro-1-naphthol, dehydrated by Al₂O₃ at 160°/high vac. to 1-C₁₀H₇Et (picrate, m.p. 98°). Under identical conditions (I) is dehydrogenated to 1-acetylenyl-3:4-dihydronaphthalene, b.p. 118°/10 mm. 6-Methoxy-1-acetylenyl-3:4-dihydronaphthalene, b.p. 120°/0.1 mm., obtained by distilling in a high vac. the product of the interaction of (II) and 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene, is reduced (H₂-Pd-CaCO₃ in EtOH-dioxan) to the vinyl compound, which with (CH₃CO)₂ in abs. C₆H₆ at 110—115° forms isomeric adducts, C₁₉H₂₂O₃, m.p. 174—175° (III) and 107—108°, both of which are reduced (H₂-Pd-CaCO₃ in EtOAc) to 7-methoxy-1:2-diacetyl-1:2:3:4:9:10:11:12-octahydrophenanthrene (IV), m.p. 127—128°. (III) in C₆H₆ is cyclised by NaOMe-MeOH to 15-methyl-15-dehydro-x-norequilenin *Me* ether (V) or (VI), m.p. 116—117°, whereas (IV) yields 15-methyl-15-dehydro-x-norœstrone *Me* ether (VII; R = Me), m.p. 181—183° (oxime, m.p. 185—186°), or

its isomeride (VIII). (VII) or (VIII) is hydrolysed to 15-methyl-15-dehydro-x-norœstrone, m.p. ~180°, or

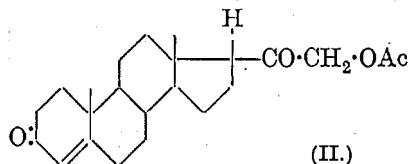


its isomeride [(VII) and (VIII) with R = H] which has œstrogenic activity. H. W.

Steroids and sex hormones. LXIV. Preparation of *D*-homodihydrotestosterone. M. W. GOLDBERG and R. MONNIER (Helv. Chim. Acta, 1940, 23, 840—845).—3-*trans*-Acetoxy-*D*-homoandrostane-17 α -one is reduced (H₂-PtO₂ in AcOH at room temp.) to *D*-homoandrostane-3-*trans*-17 α -diol 3-acetate, m.p. 160—167° (mixture of *cis-trans* isomerides at C_(17 α)), which with BzCl in C₅H₅N affords the 17 α -benzoate, m.p. 201—202°. This is hydrolysed by KHCO₃ in MeOH to *D*-homoandrostane-3-*trans*-17 α -diol 17 α -benzoate, m.p. 230—233°, oxidised (CrO₃ in AcOH) to *D*-homoandrostane-17 α -ol-3-one 17 α -benzoate, m.p. 194—195°, hydrolysed (KOH-MeOH) to *D*-homoandrostane-17 α -ol-3-one (*D*-homodihydrotestosterone) (I), m.p. 187—189°. All m.p. are corr. (vac.). The physiological activity of (I) is equal to that of dihydrotestosterone. H. W.



Constituents of the adrenal cortex and related substances. XL. 17-isoDeoxycorticosterone. C. W. SHOPPEE (Helv. Chim. Acta, 1940, 23, 925—934).—Δ⁴-Pregnene-17β:20:21-triol-3-one is converted by Ac₂O and C₆H₅N at room temp. into the 20:21-diacetate (I), m.p. 170—172° and, after re-



solidification, m.p. 193—194°. With Zn dust in boiling C₅H₅N, (I) gives 17-isoDeoxycorticosterone acetate (II), m.p. 137—138°, [α]_D²⁵ -21°±3° in COMe₂, whereas in boiling PhMe a polymorph (III), m.p. 174°, [α]_D²⁵ -26°±2°, [α]_D²⁵ -32°±2° in COMe₂, is produced. (II) or (III) is transformed by boiling conc. HCl-EtOH followed by acetylation into deoxycorticosterone acetate, m.p. 159—161°, [α]_D²⁵ +182°±4°, [α]_D²⁵ +221°±3° in EtOH, and hydrolysed by KHCO₃ in aq. MeOH at room temp. to isoDeoxycorticosterone, m.p. 179—181°, [α]_D²⁵ -6°±2°, [α]_D²⁵ -9°±2° in abs. EtOH, oxidised by HIO₄ in aq. MeOH at 20° to iso-3-ketoœtio-Δ⁴-cholenic acid (IV), m.p. 194—196°, [α]_D²⁵ +47.5°±2°, [α]_D²⁵ +54°±3° in COMe₂ [*Me* ester (V), m.p. 115—116°, [α]_D²⁵ +36°±2°,

$[\alpha]_{401}^{20} + 46^\circ \pm 3^\circ$ in COMe_2 . Isomerisation does not occur when (IV) is heated with conc. HCl-AcOH (1:9) at 100° or when (V) is boiled with KOH-MeOH . M.p. are corr. H. W.

Nature of the by-product in the synthesis of vitamin- K_1 . M. TISHLER, L. F. FIESER, and N. L. WENDLER (J. Amer. Chem. Soc., 1940, **62**, 1982—1991).—The by-product isomeric with 2-methyl-3-phytyl-1:4-naphthaquinol (I) (A., 1939, II, 513; 1940, II, 96) is 2-methyl-2-phytyl-2:3-dihydro-1:4-naphthaquinone (II). Figures given in parentheses below are $\log E_{\text{mol.}}$. Variations in the synthesis lead to 15–24% of (I) and 20–22% of (II). (II) is not formed from (I) (cf. *loc. cit.*), since >90% of (I) is recovered after heating with $\text{H}_2\text{C}_2\text{O}_4$ in dioxan for 34 hr. at 75° . (II) is insol. in Claisen's alkali, does not reduce $\text{AgNO}_3\text{-EtOH}$, gives neither the Furter-Meyer nor the Craven test, absorbs $\sim 2 \text{ H}_2$ in presence of PtO_2 , absorbs Br in CCl_4 , does not react with CH_3N_2 , MgMeBr at 180° , AlBr_3 , or various other reagents, and is unchanged by HCl-AcOH at 100° . It gives a 2:4-dinitrophenylhydrazone, m.p. $107\text{--}108^\circ$, is pyrolysed (best) in boiling decahydronaphthalene and N_2 to vitamin- K_1 (5%) and 2-methyl-1:4-naphthaquinol (10%), and has absorption max. at 253 (3.97) and 300 μ . (3.27). It is oxidised by Pb(OAc)_4 or SeO_3 . With $\text{CrO}_3\text{-AcOH}$ at $60\text{--}70^\circ$ it gives 2-methyl-2:3-dihydro-1:4-naphthaquinone-2-acetic acid, m.p. 126° , and $\zeta\alpha\zeta$ -trimethylpentadecan- β -one (identified as semicarbazone). It is reduced by $\text{Al(OPr}^i)_3\text{-Pr}^i\text{OH-CCl}_4\text{-HgCl}_2$ to 1:4-dihydroxy-2-methyl-2-phytyl-1:2:3:4-tetrahydronaphthalene, m.p. $\sim 40\text{--}50^\circ$ (diacetate, an oil; bis-2:5-dinitrobenzoate, forms, m.p. $74\text{--}75^\circ$ and 120° ; 2 active H), dehydrated by conc. HCl-AcOH at room temp. to a mixture including a little 2- $\text{C}_{10}\text{H}_7\text{Me}$. Vitamin- K_1 with SnCl_2 in boiling HCl-AcOH gives the naphthotocopherol (III), b.p. 155° (liquid)/ 10^{-5} mm. [p-nitrobenzoate, m.p. $84\text{--}85^\circ$; absorption max. 246 (4.54) and ~ 320 μ . (3.6)]; this is oxidised by $\text{FeCl}_3\text{-H}_2\text{O-MeOH-Et}_2\text{O}$ to 2-methyl-3- γ -hydroxy- $\beta\gamma$ -dihydrophytyl-1:4-naphthaquinone (IV) [quinol di- (V), m.p. $\sim 20^\circ$, and triacetate, m.p. 65°]. 2:3:1:4- $\text{C}_{10}\text{H}_4\text{Me}_2(\text{OH})_2$, phytol, and $\text{H}_2\text{C}_2\text{O}_4$ in dioxan at 75° give 2:3-dimethyl-2-phytyl-2:3-dihydro-1:4-naphthaquinone, b.p. $140\text{--}150^\circ/10^{-4}$ mm. [absorption max. 253 (3.96) and ~ 300 μ . (3.2); consumes 2 MgMeI ; absorbs 4 H with $\text{Al(OPr}^i)_3$]. The by-product, $\text{C}_{19}\text{H}_{20}\text{O}_2$, m.p. 73° (A., 1940, II, 17) is probably 2-methyl-2- $\beta\gamma$ -dimethylbutenyl-2:3-dihydro-1:4-naphthaquinone; it has absorption max. at 253 (3.98) and 298 μ . (3.31) [cf. (II)]; its solubility in alkali is ascribed to enolisation. The following absorption max. are recorded: 2-methyl-1:4-naphthaquinol Et_1 ether, m.p. $115\text{--}116^\circ$, 243 (4.26) and ~ 320 μ . (3.7); 1-hydroxy-4-keto-1-phenyl-2:3-dimethyl-1:4-dihydronaphthalene (Crawford, A., 1940, II, 82) 251 (4.07) and 281 μ . (3.91); 2-methyl-3-phytyl-, 248 μ . (4.26), and 2:3-diallyl-1:4-naphthaquinone, 249 μ . (4.24); vitamin- K_1 248 μ . (4.24–4.27) in EtOH . (III) has vitamin-E activity in 25-mg. and -K activity in 0.3–0.6-mg. doses (18 hr.); (IV) and (V) have no -K activity. (II) has -K activity in 5×10^{-5} -g. doses. R. S. C.

Pigments from sea-urchins and syntheses of related compounds. C. KURODA and H. OHSHIMA (Proc. Imp. Acad. Tokyo, 1940, **16**, 214–217).—The spines of *Pseudocentrotus depressus* ("Aka-uni") when treated with mineral acid and org. solvent give the pigment *spinochrome-Aka*, sublimes at $285\text{--}295^\circ$, identified as 2:3:5:7:8-pentahydroxy-6-methyl-1:4-naphthaquinone (2:3:7- Me_3 ether, m.p. 160° ; penta-acetate, m.p. 182°). The spines of *Heterocentrotus mammillatus* and *Anthocardis crassispina* give the pigments *spinochrome-F*, m.p. 229° , and -*M*, m.p. 193° , respectively. 2:3:1:4-(OMe) $_2\text{C}_6\text{H}_2(\text{OH})_2$ with methylmaleic anhydride and $\text{AlCl}_3\text{-NaCl}$ gives 2:3:5:8-tetrahydroxy-6-methyl-1:4-naphthaquinone, m.p. 230° (tetra-acetate, m.p. $178\text{--}179^\circ$; 2:3- Me_2 ether, m.p. 117°); similarly, (CH_3CO) $_2\text{O}$ gives 2:3:5:8-tetrahydroxy-1:4-naphthaquinone, m.p. 265° (cf. A., 1939, II, 513) (tetra-acetate, m.p. 207° ; 2:3- Me_2 ether, m.p. 129°). E. W. W.

Preparation of halogenoaminoanthraquinones.—See B., 1940, 726.

Application of the diene synthesis to terpenoid compounds. Eucarvone and maleic anhydride. T. F. WEST (J.C.S., 1940, 1162–1164).—Eucarvone [2:4-dinitrophenylhydrazone, m.p. $152\text{--}153^\circ$ (decomp.)] with (CH_3CO) $_2\text{O}$ forms an adduct, $\text{C}_{14}\text{H}_{16}\text{O}_4$, m.p. $165\text{--}167^\circ$ (Me_2 , m.p. $102\text{--}103^\circ$, and Et_2 esters, m.p. $93\text{--}95^\circ$). These results invalidate one of the arguments used by Goodway and West (A., 1939, II, 79) to criticise Rydon's seven-membered ring structure for caryophyllene. F. R. S.

Dehydrogenation. IV. Catalytic disproportionation and dehydrogenation of some terpenes and terpene ketones. R. P. LINSTEAD, K. O. A. MICHAELIS, and S. L. S. THOMAS (J.C.S., 1940, 1139–1147).—The results of the action of Pd and Pt catalysts on the compounds are in harmony with the known structures and under mild conditions give clear evidence of the skeleton structure and the no. of double bonds. All the unsaturated substances undergo disproportionation into aromatic and saturated compounds at comparatively low temp. ($140\text{--}205^\circ$), the proportions formed being those predictable from the no. of double bonds in the original terpene. Limonene gives a mixture of *p*-cymene and *p*-menthane in mol. ratio $\sim 2:0.9$ at 140° (Pt-C). Pinene at 156° with Pt-C affords equimol. proportions of *p*-cymene and pinane. Cadinene at 180° (Pt-C) yields cadalene and tetrahydrocadinene, but under vigorous conditions 1:6- $\text{C}_{10}\text{H}_6\text{Me}_2$ is obtained. At 205° with Pd-C, selinene is converted into eudalene and tetrahydroselinene. Pulegone with Pd-C at 175° forms menthone and thymol. Carvone is isomerised almost quantitatively to carvacrol. All the compounds studied, whether unsaturated or saturated (with the exception of camphor, which is completely resistant), give their aromatic counterparts with elimination of H at higher temp. F. R. S.

Mutarotation of α -nitrocamphor in chlorobenzene solution.—See A., 1940, 1, 416.

Triterpene resinols and related acids. IX. Oxidation of α -amyradienyl acetate. E. S. EWEN and F. S. SPRING. X. β -Amyradienol. C. W.

PICARD and F. S. SPRING (J.C.S., 1940, 1196—1198, 1198—1202).—IX. Ozonisation of α -amyradienyl acetate (I) at 0° gives a mixture of α -amyrenonyl acetate and epi(iso)- α -amyrenonyl acetate (II), $C_{32}H_{50}O_3$, m.p. 199—200°, $[\alpha]_D^{20} +56^\circ$ in $CHCl_3$, which is reduced ($Na-C_5H_{11}\cdot OH$) followed by treatment with Ac_2O to (I). Ozonisation of (I) at 22° affords a mixture containing an amorphous acid fraction, (II), and α -amyradienyl acetate, $C_{32}H_{50}O_4$, m.p. 257—258°, $[\alpha]_D^{21} +120^\circ$ in $CHCl_3$.

X. Prolonged treatment of β -amyrenonyl benzoate, $[\alpha]_D^{20} +156^\circ$ in $CHCl_3$, with KOH (cf. Beynon *et al.*, A., 1938, II, 416; Ruzicka *et al.*, A., 1939, II, 330) gives a low-melting β -amyrenonol, probably contaminated with an isomeric $\alpha\beta$ -unsaturated ketone. Purification cannot be achieved by crystallisation but is effected by acetylation, pure β -amyrenonyl acetate, $[\alpha]_D^{20} +116^\circ$ in $CHCl_3$, then being readily isolated. Reduction of β -amyrenonol with $Na-EtOH$ gives an addition-reduction compound, $C_{32}H_{56}O_2$, m.p. 236.5—239.5°, and with $Na-C_5H_{11}\cdot OH$ affords a similar compound, $C_{35}H_{62}O_3$, m.p. 238—239°; with Ac_2O these compounds yield β -amyradienyl acetate. Hydrolysis of the latter leads to β -amyradienol, m.p. 213.5—214.5°, $[\alpha]_D^{20} +319^\circ$ in $CHCl_3$ (benzoate, m.p. 250°, $[\alpha]_D^{20} +317^\circ$ in $CHCl_3$), which is oxidised ($AcOH-CrO_3$) to β -amyradienone, m.p. 206—208°. The benzoate on reduction with $Na-C_5H_{11}\cdot OH$ and treatment with Ac_2O gives an acetate, $C_{35}H_{62}O_3$, m.p. 223—224°, which is a mixed crystal containing β -amyradienyl acetate and β -amyrenyl acetate and corresponds with the "dehydro- β -amyrenyl acetate b" of Simpson (cf. A., 1940, II, 137). F. R. S.

Constituents of *Helenium* species. IV. The compound, m.p. 233—234°, obtained from *H. tenuifolium*. E. P. CLARK (J. Amer. Chem. Soc., 1940, 62, 2154—2156; cf. A., 1940, II, 184).—Rast's method of determining mol. wt. is unreliable in the tenulin series. The substance, $C_{16}H_{22}O_6$, m.p. 233—234° (A., 1939, II, 435), is really *tenulin* β -methoxyethyl ether, $C_{19}H_{26}O_6$. It gives an *ethoxyacetyl* derivative, m.p. 119°, analysis of which indicates the mol. wt. With $H_2O_2-NaOH-H_2O-COMe_2$ or $KMnO_4-COMe_2-H_2O$ it gives an *acid*, $C_{19}H_{26}O_9$, m.p. 239° (*Me* ester, m.p. 283°), hydrolysed by boiling, dil. acid to $OMe[CH_2]_2\cdot OH$ and acetyltenulinic acid, m.p. 239° or (? anhyd.) 319°. The OH and Ac of *tenulin* are sterically proximate. R. S. C.

Constituents of the leaves of certain *Leucadendron* species. III. Oxidations of leucodrin derivatives with periodic acid and lead tetracetate. W. S. RAPSON (J.C.S., 1940, 1271—1274).—Oxidation of leucodrin *Me* ether (I) in the lactonic form in acid media with either $Pb(OAc)_4$ or HIO_4 results in absorption of 2 equivs. of O and formation of 1 equiv. of CH_2O . In 0.1N-NaOH, oxidation of (I) or leucodrin (II) with excess of HIO_4 leads to absorption of 8 equivs. of O and gives 1 equiv. of CH_2O and anisylsuccinic acid in optically active form; with $Pb(OAc)_4$ and (I), 15 equivs. of O are absorbed. Oxidation of leucodrin *Me* ether with $Pb(OAc)_4$ in alkaline solution affords a monobasic *acid*, $C_{18}H_{26}O_8 (+H_2O)$, m.p. 73—76.5°, and the Br-ether similarly gives a substance, $C_{18}H_{25}O_8Br$, m.p. 178°

(decomp.). Mutarotation of (II) in aq. or aq.-EtOH media has not been observed, indicating that the lactone ring systems are fairly stable; acidification of alkaline solutions of (I) or (II) causes the $[\alpha]$ to revert during 80—100 hr. to that of the corresponding lactonic forms. Interpretation of the results in terms of a full structure for (II) has not been possible but the partial structure $p-OH\cdot C_6H_4\cdot CH(CH_2\cdot CO\cdot O\cdot)\cdot C_5H_8O_3\cdot CO\cdot O\cdot$ is suggested. F. R. S.

Hydroxy-lactone from *d*-pimaric acid. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1940, 62, 2044—2047).—*d*-Pimaric acid (I) and conc. H_2SO_4 at -20° to -30° give a saturated OH-lactone, $C_{20}H_{32}O_3$, m.p. 181—182°, b.p. 200—250° (bath)/1 mm., $[\alpha]_D^{20} -4^\circ$ in abs. EtOH, only partly hydrolysed by $NaOH-EtOH$ but converted by $KOH-Bu^tOH$ into the corresponding *acid*, $+0.66H_2O$, m.p. 150—151°, and anhyd. (*Me* ester, m.p. 156—157°). Known tests are used to detect dihydro-*l*-pimaric and -abietic and *l*-abietic (II) acid in (I). When freed (method described) from (II) but still containing H_2 -acids, (I) has m.p. 218—219°, $[\alpha]_D^{20} +75^\circ$ in abs. EtOH. (I) has never been obtained pure. On the assumption that H_2SO_4 converts (I) into 50% each of acid and neutral material, and by isolation of the latter, it is shown that $>10\%$ and $>14\%$ of (I) is present in the oleoresin and rosin of *P. palustris* and *P. caribaea*, respectively. Analysis of mixtures of (I) and *l*-pimaric acid gives slightly high results (within 5—10%) for (I). R. S. C.

Kikyo root. X. Constitution of platycodigenin. Properties of double linking and oxygen atoms of platycodigenin. M. TSUJIMOTO (J. Agric. Chem. Soc. Japan, 1940, 16, 613—620; cf. A., 1939, II, 556).—Platycodigenin contains one double linking which cannot be reduced catalytically, and of the 7 O, two are present as CO_2H , and four as OH. J. N. A.

Lignin and related compounds. I. Hydrogenation of soft-wood lignin. Y. HACHIYAMA, S. ZYODAI, and M. UMEZU (J. Soc. Chem. Ind. Japan, 1940, 43, 127B).—Lignin (from *Picea jezoensis*) was hydrogenated (NiO catalyst in dioxan; 35—55 hr. at 260—270°/95—230 atm.); the Et_2O -sol. products included 1:4:3- $C_6H_3Pr(OH)(OH)\cdot OMe$ (I), 1:2:4- $C_6H_3(OH)_2\cdot CO_2H$, *o*- $C_6H_4(OH)_2$, and *p*- $OH\cdot C_6H_4\cdot CO_2H$. (I) is an important constituent of soft-wood lignin. R. T.

Lignin. XXXIV. Formation of vanillin from spruce lignin. K. FREUDENBERG, W. LAUTSCH, and K. ENGLER (Ber., 1940, 73, [B], 167—171).—Spruce lignin (I), or, better, deresinated spruce-wood powder, in 2N-NaOH with $PhNO_2$ at 160° (3 hr.) gives, after removal of $PhNO_2$, NH_2Ph , and Ph_2N_2O , neutralisation and treatment with $NaHCO_3$, and extraction with C_6H_6 , vanillin (II) = 20—25% of original (I). Other products include phenols, vanillic and veratric acids, $AcOH$, $H_2C_2O_4$, and *vanillin-5-carboxylic acid*, m.p. 250° (decomp.); taking account of these, 50% of the original (I) is isolated as (II) or its breakdown products. Sulphite waste liquor may be successfully used as a source of (I) and thus of (II). E. W. W.

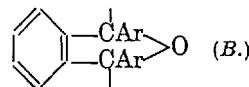
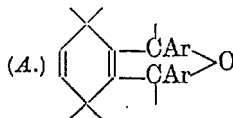
Esters of 2-furylacetic acid. J. F. RYAN, J. PLUCKER, tert., and E. D. AMSTUTZ (J. Amer. Chem. Soc., 1940, 62, 2037).—*Me*, b.p. 87–88°/21 mm., *Et*, b.p. 88°/15 mm., *Pr^a*, b.p. 115–116°/34 mm., *Pr^b*, b.p. 92–93°/17 mm., *Bu^a*, b.p. 110–111°/13 mm., and *Bu^b* 2-furylacetate, b.p. 112–113°/21 mm., are prepared. R. S. C.

N'-Aryl-N-alkylfuramidines. W. M. DEGNAN and F. B. POPE (J. Amer. Chem. Soc., 1940, 62, 1960–1962).—Heating 2-furoyl chloride with NH_2R and dil. KOH (15–20% excess) gives 2-furo-*n*-propyl-, m.p. 39–40°, -*n*-, m.p. 40–41°, -sec-, m.p. 122–123°, and -tert-butyl-, m.p. 99°, -*n*-amyl-, m.p. 31–32°, - β -amyl-, m.p. 48–56°, - β -methyl-sec-butyl-, m.p. 68–69°, -isoamyl-, m.p. 53–54°, -8-methyl- β -amyl-, m.p. 54–55°, -cyclohexyl-, m.p. 108.5–109°, and - β -ethyl-*n*-hexyl-, an oil, -amide. Addition of the appropriate amide and then of $\text{NH}_2\text{R}'$ to PCl_5 in C_6H_6 gives N'-phenyl-N-*n*-propyl-, m.p. 63.5–64° (139–140°), -N-*n*-butyl-, m.p. 67–68° (141–142°), and -N-cyclohexyl-2-furamidine, m.p. 78.5–79° (174°), N'-*p*-phenetyl-N-*n*-propyl-, m.p. 81.0–81.5° [(+H₂O) 78.5–79.5°], -N-*n*-butyl-, m.p. 65.5–66° [(+H₂O) 78.5–79.5°, (anhyd.) 135–136°], -N-sec-butyl-, m.p. 52.0–52.5° (132–133°), -N-*n*-amyl-, m.p. 61.0–61.5° [(+H₂O) 75–76°], -N- β -amyl-, m.p. 75–76° (125.5–126.5°), -N-isoamyl-, m.p. 77° (120–121°), -N-8-methyl- β -amyl-, m.p. 77° (120–121°), and -N-cyclohexyl-2-furamidine, m.p. 108–109° (170–171°), N'-*p*-carbethoxyphenyl-N-*n*-propyl-, m.p. 86–87° (167–168°), -N-*n*-butyl-, m.p. 75.5–76° (128–129°), and -N-cyclohexyl-2-furamidine, m.p. 114–115° (188–189°), N'- α -, m.p. 54.5–55.5° (99–101°), and N'- β -naphthyl-N-*n*-butyl-2-furamidine, m.p. 61.5–62° (91.5–92.5°). Figures in parentheses are m.p. of the hydrochlorides, which are potent local anaesthetics.

R. S. C.

Absorption and fluorescence spectra of dihydroisobenzfurans and isobenzfurans. R. ADAMS and M. H. GOLD (J. Amer. Chem. Soc., 1940, 62, 2038–2042; cf. A., 1940, II, 280).—*trans*-($\text{p-C}_6\text{H}_4\text{Ph-CH}$)₂ (I) (modified prep.) and ($\text{CH}_2\text{-CH}$)₂ in C_6H_6 at 100° give 4 : 5-dixenylcyclohexene, m.p. 267–268°, converted by boiling $\text{H}_2\text{SO}_4\text{-Ac}_2\text{O}$ into 1 : 3-dixenyl-4 : 7-dihydroisobenzfuran, m.p. 238–239° [absorption max. 2440 (4.4), 2720 (4.45), 3620 (4.8), fluorescence max. 4290, 4845, 4965, and 5160 Å.] (figures in parentheses are log ϵ), which with Br-NaOAc-AcOH gives *o*-dixenylbenzene, m.p. 191–192°. With $\text{KOH-EtOH-H}_2\text{O-C}_6\text{H}_6\text{-Zn}$ dust this gives 1 : 3-dixenylisobenzfuran, m.p. 247–249° [absorption max. 2400 (4.4), 2920 (4.6), 3350 (3.95), and 4360 (4.55), fluorescence max. 5250 Å.]. ($\text{CH}_2\text{-CMe}_2$)₂ and (I) yield similarly 4 : 5-dixenyl-1 : 2-dimethylcyclohexene, m.p. 280–281° (decomp.), 1 : 3-dixenyl-5 : 6-dimethylisobenzfuran, m.p. 245–247° [absorption max. 2440 (4.4), 2960 (4.6), 3400 (4.0), and 4350 (4.6); fluorescence max. 5250 Å.], and 4 : 7-dihydroisobenzfuran, m.p. 239–241° [absorption max. 2450 (4.4), 2710 (4.45), and 3670 (4.5); fluorescence max. 4290, 4915, 5025, and 5250 Å.], and 4 : 5-dixenyl-1 : 3-dimethylbenzene, m.p. 218–219°. The following absorption (a) and fluorescence max. (b) are recorded. 1-3-Diphenyl-4 : 7-dihydroisobenzfuran (a) 2300 (4.4),

3320 (4.7), 3480 (4.55), (b) 3840 and 4050, and -isobenzfuran 2610 (4.5), 2700 (4.5), 3100 (3.95), and 4150 (4.45), (b) 4860, 1 : 3-diphenyl-5 : 6-dimethyl-4 : 7-dihydroisobenzfuran (a) 2300 (4.4), 3330 (4.65), and 3490 (4.5), (b) 3840, 4080, and 4590, and -isobenzfuran (I) (a) 2490 (4.3), 2580 (4.4), 2690 (4.5), 2770 (4.55), 3100 (3.95), 4150 (4.4), (b) 4860 Å. The optical data indicate existence of free radicals [as (A) and (B)], which is confirmed by the absorption of O_2 by isobenzfurans and by addition of $\alpha\beta$ -unsaturated CO-compounds preceded by a transitory red colour. The



dimeride of (I) (Guyot *et al.*, A., 1907, i, 76) is probably formed by union of 2 mols. of (B). M.p. are corr.

R. S. C.

Condensation products of phenols and ketones.
V. Structure of the dimeric forms of *o*-isopropenylphenols. W. BAKER and D. M. BESLY (J.C.S., 1940, 1103–1106).—Condensation of *m*-cresol with COMe_2 in presence of HCl gives the dimeride of 4-isopropenyl-*m*-cresol, which is regarded as 2'-hydroxy-2 : 4 : 4 : 7 : 4'-pentamethylflavan (I), the Et_2O addition product, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{-Et}_2\text{O}$, having m.p. 76–77°. (I) with Ac_2O forms 2'-acetoxy-2 : 4 : 4 : 7 : 4'-pentamethylflavan, m.p. 108°; it is oxidised ($\text{KMnO}_4\text{-Ac}_2\text{O}$) to 2 : 4 : 4 : 7-tetramethylchroman-2-carboxylic acid, m.p. 148–149°. The oxidation and a consideration of the mechanism of its formation lead to the structure assigned. 2-Hydroxy-5-methylacetophenone, $\text{C}_5\text{H}_5\text{N}$, and *o*- $\text{OMe-C}_6\text{H}_4\text{-COCl}$ followed by HCl give 2-(2'-methoxybenzoyloxy)-5-methylacetophenone, m.p. 85°, which with K_2CO_3 affords ω -2'-methoxybenzoyl-2-hydroxy-5-methylacetophenone, m.p. 106°, converted by AcOH-NaOAc into 2'-methoxy-6-methylflavone, m.p. 110°. Hydrolysis (HBr) of this compound leads to 2'-hydroxy-6-methylflavone, m.p. 255–256° (*Ac* derivative, m.p. 101°). *o*- $\text{OH-C}_6\text{H}_4\text{-COMe}$, $\text{C}_5\text{H}_5\text{N}$, and *o*- $\text{OMe-C}_6\text{H}_4\text{-COCl}$ give 2-(2'-methoxybenzoyloxy)acetophenone, m.p. 79°, similarly successively converted into ω -2'-methoxybenzoyl-2-hydroxyacetophenone, m.p. 80°, 2'-methoxy- and 2'-hydroxyflavone. The last compound and the 6-Me derivative give mixtures on catalytic reduction.

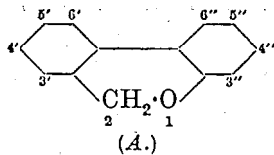
F. R. S.

Isolation of cannabinol, cannabidiol, and quebrachitol from red oil of Minnesota wild hemp. R. ADAMS, D. C. PEASE, and J. H. CLARK (J. Amer. Chem. Soc., 1940, 62, 2194–2196).—Steam-distillation of marihuana red oil (I) (Adams *et al.*, A., 1940, II, 80), fractional distillation in vac., removal of cannabinol (II) as bisdinitrobenzoate (III) (47%) and later by pyrolysis with $\text{C}_5\text{H}_5\text{N-HCl}$ at 225–230°/75–100 mm., conversion of the non-volatile, alkali-insol. part of the residue by 3 : 5 : 1-(NO_2)₂ $\text{C}_6\text{H}_3\text{-CON}_3$ into urethanes, and fractional crystallisation and decomp. of the least sol. fraction by $\text{NH}_3\text{-EtOH}$, gives cannabinol, m.p. 75–76° (corr.), b.p. 185°/0.5 mm. (lit., an oil) [3 : 5-dinitrophenylurethane, m.p. 221–222° (decomp.); *p*-nitrobenzoate, new m.p. 165–166°; *m*-nitrobenzenesulphonate, new m.p. 127–129°; acetate, new m.p. 76–77°]. Ammonolysis of (III)

gives (II), m.p. 66—67° (corr.) (lit., an oil), $[\alpha]_D^{27} -125^\circ$ in EtOH. Extraction of (I) with H₂O gives quebrachitol.

R. S. C.

Structure of cannabinol. I. Preparation of an isomeride, 3-hydroxy-6:6:9-trimethyl-1-*n*-amyl-6-dibenzopyran [4''-hydroxy-2:2:5'-trimethyl-6''-*n*-amyl-6-dibenzopyran]. R. ADAMS, D. C. PEASE, J. H. CLARK, and B. R. BAKER. **II. Synthesis of two isomerides, 4''-hydroxy-2:2:5'-trimethyl-3''- and -5''-*n*-amyl-6-dibenzopyran.** R. ADAMS, C. K. CAIN, and B. R. BAKER. **III. Synthesis of cannabinol, 6''-hydroxy-2:2:5'-trimethyl-3''-*n*-amyl-6-dibenzopyran.** R. ADAMS, B. R. BAKER, and R. B. WEARN. **IV. Synthesis of two additional isomerides containing a resorcinol residue.** R. ADAMS and R. B. BAKER (J. Amer. Chem. Soc., 1940, **62**, 2197—2200, 2201—2204, 2204—2207, 2208—2215).—I. *o*-C₆H₄Br·CO₂H (I), *m*-C₆H₄(OH)₂ (II), CuSO₄, and aq. NaOH give 4''-hydroxydibenzopyrone (numbering as A) (52%), new m.p. 247° (Me ether, new m.p. 143°; acetate, m.p. 177°), converted by MgMeI into 4''-hydroxy-2:2-dimethyldibenzopyran (40%), m.p. 128° (acetate, m.p. 96°).



Orcinol and (I) similarly give 4''-hydroxy-6''-methyl-6-dibenzopyrone, softens at 143°, m.p. 150°, and 4''-hydroxy-2:2:6''-trimethyldibenzopyran, m.p. 144° (acetate, m.p. 85°). 4:2:1-C₆H₃MeBr·CO₂H (IV) and (II) give 4''-hydroxy-5':6''-dimethyldibenzopyrone, m.p. 311° (block) (acetate, m.p. 175—176°). Orcinol and (IV) give 4''-hydroxy-5'-methyl-6''-*n*-amyl-6-dibenzopyrone (V) (25%), m.p. 206° (acetate, m.p. 126°), and 4''-hydroxy-2:2:5'-trimethyl-6''-*n*-amyl-6-dibenzopyran (VI), m.p. 83° [acetate (VII), m.p. 62°; *p*-nitrobenzoate, m.p. 92°; *m*-nitrobenzenesulphonate, m.p. 118°]. The orientation of (V) and (VI) depends on non-identity with cannabinol (see below).

II. 7-Hydroxy-4-methylcoumarin and Bu^cCOCl in boiling C₅H₅N give the 7-valeroxy-compound, m.p. 75—76°, which with AlCl₃ at 80° and later 150° gives 7-hydroxy-8-*n*-valeryl-4-methylcoumarin, m.p. 98—103°, which in 16% aq. NaOH-N₂ gives 2:6-dihydroxy-valerophenone, m.p. 85—86°. Zn-Hg-HCl-H₂O-EtOH then gives 2-*n*-amylresorcinol (VIII), m.p. 55—56°, but in absence of EtOH the BuCO is eliminated. (IV), (VIII), aq. NaOH, and CuSO₄ give 4''-hydroxy-5'-methyl-3''-*n*-amyl-6-dibenzopyrone, m.p. 238—239° (decomp.), converted by MgMeI into 4''-hydroxy-2:2:5'-trimethyl-3''-*n*-amyl-6-dibenzopyran, m.p. 87·5—88·5° [*p*-nitro-, m.p. 120—121°, and thence (H₂-PtO₂; EtOH; 2—3 atm.) *p*-amino-benzoate, m.p. 165·5—166·5°; *m*-nitrobenzenesulphonate, m.p. 122·5—123°; acetate, an oil]. 4-*n*-Amylresorcinol and (IV) give similarly 4''-hydroxy-5'-methyl-5''-*n*-amyl-6-dibenzopyrone, m.p. 226°, and 4''-hydroxy-2:2:5'-trimethyl-5''-*n*-amyl-6-dibenzopyran, m.p. 86—88° [acetate (IX), m.p. 68—69°; 4''-*m*-nitrobenzenesulphonate, m.p. 100—101°; *p*-nitrobenzenesulphonate, an oil]. Similarity in the absorption spectra of (VII), (IX), and cannabinol acetate confirms the dibenzopyran structure of cannabinol.

III. Menthone, (IV), NaOEt, and Cu(OAc)₂ in boiling EtOH give 6''-keto-4'':4''-dimethyl-3'':4'':5'':6''-tetrahydrodibenzopyrone, m.p. 145—146°. *n*-C₅H₁₁·CHO (X), COMe₂, and 10% NaOH give COMe·CH·CH·C₅H₁₁·*n* (46%), b.p. 124—125°/32 mm., which with CH₂(CO₂Et)₂ and NaOEt-EtOH gives an ester, converted by hydrolysis (KOH) and heating in HCl into 5-*n*-amylcyclohexane-1:3-dione (XI), m.p. 70—71°, also obtained from olivetol by H₂-Raney Ni in aq. NaOH at 125°/2800 lb. (XI), (IV), and NaOEt-Cu(OAc)₂-EtOH give 6''-keto-5'-methyl-4''-*n*-amyl-3'':4'':5'':6''-tetrahydrodibenzopyrone (78%), m.p. 95—96°, dehydrogenated by S at 250° to 6''-hydroxy-5'-methyl-4''-*n*-amyl-6-dibenzopyrone (34%), m.p. 186°, which with MgMeI affords cannabinol [6''-hydroxy-2:2:5'-trimethyl-4''-*n*-amyl-6-dibenzopyran], m.p. 76—77°. Commercial (X) contains CHET₂·CHO and leads by the above methods to 5- α -ethyl-*n*-propylcyclohexane-1:3-dione, m.p. 104—105°, 6''-keto-5'-methyl-4''- α -ethyl-*n*-propyl-3'':4'':5'':6''-tetrahydrodibenzopyrone, m.p. 111—112°, 6''-hydroxy-5'-methyl-4''- α -ethyl-*n*-propyldibenzopyrone, m.p. 217—218° (acetate, m.p. 128—130°), and 6''-hydroxy-2:2:5'-trimethyl-4''- α -ethyl-*n*-propyldibenzopyran, m.p. 133—134° (acetate, m.p. 103°; *p*-nitrobenzoate, m.p. 171°).

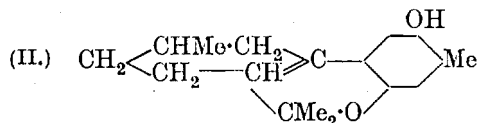
IV. 4-*n*-Amyldihydroresorcinol (prep. by H₂-Raney Ni at 125°/2800 lb.), m.p. 67° (IV), NaOEt, and Cu(OAc)₂ in EtOH give 6''-keto-5'-methyl-3''- (XII) (20%), m.p. 97—99°, and 5''-*n*-amyl-3'':4'':5'':6''-tetrahydrodibenzopyrone (XIII) (33%), m.p. 65—66°, separated by solvents. Reactions below show (XII) and (XIII) to be equilibrated by acid or alkali. When (XII) or (XIII) is treated with Br·CHCl₃ and the product is heated in quinoline at 200°, 6''-hydroxy-5'-methyl-3''- (XIV), m.p. 176—177°, and 5''-*n*-amyl-6-dibenzopyrone (XV), m.p. 182—183°, respectively, are obtained. (XIV), but not (XV), is obtained also by S at 250—255°. MgMeI converts (XV) into 2':6'-dihydroxy-5-methyl-2- α -hydroxyisopropyl-3'-*n*-amyl-2-phenyl, m.p. 103—104°. With *n*-NaOMe and Me₂SO₄, (XIV) or (XV) gives 6''-methoxy-5'-methyl-3''-*n*-amyl-6-dibenzopyrone (XVI), m.p. 96°, and with CH₂PhCl-NaOMe-MeOH either gives 6''-benzyloxy-5'-methyl-3''-*n*-amyl-6-dibenzopyrone (XVII), m.p. 121—121·5°, hydrolysed by boiling conc. HCl-AcOH to (XIV). However, by condensation by K₂CO₃ in COMe₂ (XIV) and (XV) give distinct derivatives, (XV) thus yielding 6''-methoxy- (XVIII), m.p. 45—46°, and 6''-benzyloxy-5'-methyl-5''-*n*-amyl-6-dibenzopyrone (XIX), m.p. 86°. 6''-Benzenesulphonoxy-5'-methyl-3''-, m.p. 103—104°, and 5''-*n*-amyl-6-dibenzopyrone, m.p. 139°, are obtained by PhSO₂Cl in boiling C₅H₅N. If crude mixed (XII) and (XIII) are subjected to Br-quinoline, 37% of (XV) is readily isolated and the mother-liquors yield 23% of (XVII). MgMeI converts (XVI) in boiling Et₂O-C₆H₆ into a carbinol, dehydrated by anhyd. MgSO₄ in boiling C₆H₆ to 6''-methoxy-2:2:5'-trimethyl-3''-*n*-amyl-6-dibenzopyran (XX), m.p. 75—76°. (XVII) gives similarly 6''-benzyloxy-2:2:5'-trimethyl-3''-*n*-amyl-6-dibenzopyran (XXI), m.p. 74—75°, by way of 2'-hydroxy-6'-benzyloxy-5-methyl-3'-*n*-amyl-2- α -hydroxyisopropyl-3-*n*-amyl-2-phenyl, m.p. 73—74°, which with Me₂SO₄-KOH-MeOH gives 6'-benzyloxy-2'-methoxy-5-methyl-3'-*n*-amyl-2-isopropenyldiphenyl, m.p.

76—77°. Hydrolysis of (XX) by HBr-AcOH or of (XXI) by conc. HCl-AcOH gives 6''-hydroxy-2 : 2 : 5'-trimethyl-3''-n-amylidibenzopyran, m.p. 62—63° (acetate, m.p. 72—73°; p-nitrobenzoate, m.p. 144°). MgMeI converts (XVIII) and (XIX) into 6'-hydroxy-2'-methoxy- (XXII), m.p. 102—103°, and -2'-benzyloxy- (XXIII), m.p. 106.5—107.5°, -5-methyl-2- α -hydroxyisopropyl-3'-n-amylidiphenyl. 48% HBr-C₆H₆ cyclises (XXIII) to 6'-benzyloxy- (XXIV), m.p. 67—68°, and (XXII) to 6'-methoxy-2 : 2 : 5'-trimethyl-5''-n-amylidibenzopyran (XXV), b.p. 182°/3 mm. p-NO₂-C₆H₄-COCl and (XXIII) in C₆H₆N give 2'-benzyloxy-6'-p-nitrobenzyloxy-5-methyl-3'-n-amyl-2-isopropenyldiphenyl, m.p. 100—101°. 6''-Hydroxy-2 : 2 : 5'-trimethyl-5''-n-amylidibenzopyran, b.p. 203—205°/3 mm. (p-nitrobenzoate, m.p. 129—130°), is obtained from (XXIV) by HCl-AcOH or from (XXV) by HBr-AcOH. M.p. (all parts) are corr. R. S. C.

Structure of cannabidiol. V. Position of the alicyclic ethylenic linkings. R. ADAMS, H. WOLFF, C. K. CAIN, and J. H. CLARK (J. Amer. Chem. Soc., 1940, 62, 2215—2219; cf. A., 1940, II, 304).—Hydrogenation (PtO₂) of cannabidiol Me₂ ether (I) in EtOH gives dihydrocannabidiol Me₂ ether (II), b.p. 158—161°/2 mm., [α]_D²⁵ -133° in 95% EtOH. Addition of m-C₆H₄(OH)₂ and then of pulegone to LiBu⁺ in Et₂O-N₂ gives a partly dehydrated carbinol, converted by KHSO₄ at 140° into 2-3'-methyl-6'-isopropylidene- $\Delta^{1:2}$ -cyclohexenylresorcinol Me₂ ether (III), m.p. 75—76°, [α]_D²⁵ +56° in 95% EtOH, which with H₂-PtO₂ in EtOH (or by partial hydrogenation in AcOH) gives 2 : 3'-methyl-6'-isopropylidene-cyclohexylresorcinol Me₂ ether (IV), m.p. 53—54°, [α]_D²⁵ +60° in 95% EtOH. 1 : 3 : 5-C₆H₃Me(OMe)₂ yields similarly 2-3'-methyl-5'-isopropylidene- $\Delta^{1:2}$ -cyclohexenyl- (V), m.p. 81—82°, [α]_D²⁵ +37° in 95% EtOH, and -cyclohexyl-oreinol Me₂ ether (VI), m.p. 114—115°, [α]_D³⁰ +44° in 95% EtOH. Doeuvre's method (ozoneisation and determination of CH₂O formed) of determining CH₂ is not quant., but a modification (described) is a reliable qual. test. It gives 63% of CH₂O from eugenyl cinnamate, 49% from cannabidiol (VII), 41% from (I), 0 from (II) or tetrahydrocannabidiol Me₂ ether. (VII) thus contains CHMe·CH₂ and not ·CMe₂. The absorption spectrum of (II) resembles that of (IV) and (VI), but not that of (III), (V), 2-5'-methyl-2'-isopropyl- $\Delta^{1:2}$ -cyclohexenylresorcinol or oreinol Me₂ ether. The endocyclic ethylenic linking of (VII) is thus not conjugated with the aromatic nucleus. R. S. C.

Conversion of cannabidiol into a product with marihuana activity. Type reaction for synthesis of analogous substances. Conversion of cannabidiol into cannabinol. R. ADAMS, D. C. PEASE, C. K. KAIN, B. R. BAKER, J. H. CLARK, H. WOLFF, and R. B. WEARN (J. Amer. Chem. Soc., 1940, 62, 2245—2246).—C₅H₅N, HCl, HCl-EtOH, HCl-Et₂O, NH₂-SO₃H, H₃PO₄-EtOH, or ZnCl₂-EtOH isomerises cannabidiol to tetrahydrocannabinol (I), b.p. 188—190°/2.5 mm. α varies (e.g., [α]_D²⁵ -160° or [α]_D³² -240°) owing to stereoisomeric differences according to the method of prep. Dehydrogenation of (I) gives cannabinol and reduction gives hexahydrocannabinol,

b.p. 153—155°/0.1 mm., [α]_D²⁷ (always) -70°. Et 5-methylcyclohexanone-2-carboxylate, oreinol, and



POCl₃ give the pyrone, converted by MgMeI into the substance (II), m.p. 115.5—116°. (I) has marihuana activity. R. S. C.

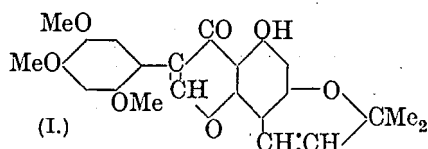
Cannabis Indica. III. Synthesis of dibenzopyran derivatives, including an isomeride of cannabinol. R. GHOSH, D. C. S. PASCALL, and A. R. TODD. IV. Synthesis of some tetrahydrodibenzopyran derivatives. R. GHOSH, A. R. TODD, and S. WILKINSON (J.C.S., 1940, 1118—1121, 1121—1125).—III. 3 : 1 : 4-NO-NAc·C₆H₃Me·CN (I), prepared from 3 : 1 : 4-NHAc·C₆H₃Me·CN and NO₂ (decomposed on keeping in C₆H₆ to 2-cyano-5-methyldiphenyl, m.p. 87—88°), with p-C₆H₄(OMe)₂ gives 2'-cyano-2 : 5-dimethoxy-5'-methyldiphenyl, m.p. 97° [-2 : 5-(OEt)₂-compound, m.p. 72—73°], which with HBr affords 6-hydroxy-5'-methyl-3 : 4-benzocoumarin, m.p. 233—234° (decomp.) (acetate, m.p. 155°). The acetate with MgMeI and PhOMe affords 5'-hydroxy-2 : 2 : 5'-trimethyldibenzopyran, m.p. 118° (acetate, m.p. 86—87°; 3 : 5-dinitrobenzoate, m.p. 169°). A corresponding series of reactions with 1 : 2 : 5-n-C₅H₁₁-C₆H₄(OMe)₂ (2-acetoxy-5-methoxyvalerophenone, m.p. 72—73°, and its semicarbazone, m.p. 159—160°, and ketazine, m.p. 161—162°) affords 2'-cyano-2 : 5-dimethoxy-5'-methyl-4-n-amylidiphenyl, b.p. 95—100°/0.036 mm., 6-hydroxy-5'-methyl-7-n-amyl-3 : 4-benzocoumarin, m.p. 191—192° (acetate, m.p. 138—139°), and 5'-hydroxy-2 : 2 : 5'-trimethyl-4''-n-amylidibenzopyran, m.p. 110—111°; the last-named substance is an isomeride of cannabinol. Oreinol Me₂ ether and (I) give 2-cyano-2' : 6'-dimethoxy-4' : 5'-dimethylazobenzene, m.p. 126°.

IV. Condensation of quinol with Et cyclohexanone-2-carboxylate (H₂SO₄) gives 6-hydroxy-3 : 4-cyclohexenocoumarin, m.p. 239—240°; the -5'-Me compound, m.p. 246°, is obtained with Et 1-methylcyclohexan-3-one-4-carboxylate, and the 7-hydroxy-5'-methyl derivative, m.p. 199—200° (lit. 142°), from m-C₆H₄(OH)₂. 5-Hydroxy-5'-methyl-7-n-amyl-3 : 4-cyclohexenocoumarin, m.p. 177°, is prepared from olivetol monohydrate. The following Ac derivatives are obtained from the OH-compound and Ac₂O in C₆H₅N : 7-acetoxy-, m.p. 185—186°, and 7-acetoxy-5'-methyl-, m.p. 132°, 6-acetoxy-, m.p. 139—140°, 5-acetoxy-7-methyl-, m.p. 124°, and 5-acetoxy-5'-methyl-7'-n-amyl-, m.p. 82—83°, -3 : 4-cyclohexenocoumarin. By condensation of the appropriate coumarin with MgMeI the following are prepared : 4''-hydroxy-2 : 2-dimethyl-, m.p. 135° (Ac derivative, m.p. 66°), 4''-hydroxy-2 : 2 : 5'-trimethyl-, m.p. 144—145° (Ac derivative, m.p. 58°), 5''-hydroxy-2 : 2-dimethyl-, m.p. 130°, 6''-hydroxy-2 : 2 : 4''-trimethyl-, m.p. 138° (Ac derivative, m.p. 107—108°), 6''-hydroxy-2 : 2 : 5' : 4''-tetramethyl-, m.p. 112—113° (Ac derivative, m.p. 124°), and 6''-hydroxy-2 : 2 : 5'-trimethyl-4''-n-amyl-, b.p. 165—175°/0.02 mm., -3' : 4' : 5' : 6'-tetrahydrodibenzo-

pyran; dehydrogenation (Pd-C) of the Ac derivative of the last compound gives cannabinal.

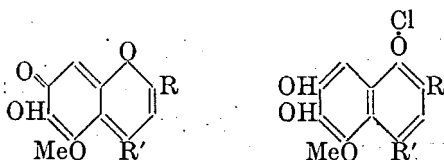
F. R. S.

Active principles of leguminous fish-poison plants. V. *Derris malaccensis* and *Tephrosia toxicaria*. S. H. HARPER (J.C.S., 1940, 1178—1184).—The resin from *D. malaccensis* has been fractionated by chemical means and pure *l*- α -toxicarol has been obtained. In addition rotenone, elliptone, deguelin, malaccol, sumatrol, and a phenol (I); $C_{23}H_{22}O_7$, m.p. 219° , $\alpha_D \pm 0^\circ$ in $CHCl_3$ (O-Ac, m.p. 210° , O-Bz, m.p. 193° , and O-Me derivatives, m.p.



178°), have been isolated. As a working hypothesis structure (I) is suggested. The resin from *T. toxicaria* has been similarly fractionated, and rotenone, *l*- α -toxicarol, and sumatrol have been isolated. F. R. S.

Constitution of santalin. J. B. LAL (Proc. Nat. Acad. Sci. India, 1939, 9, 83—88).—Previous work on santalin is reviewed, and reasons are given for assigning to it and its hydrochloride the appended formulæ:



R = 3-hydroxy-4-methoxyphenyl; R' = 4-(5-hydroxy-6-methoxy-2-*p*-methoxyphenyl-1 : 4-benzopyranyl).

A. LI.

Spectrographic study of rottlerin and its derivatives.—See A., 1940, I, 402.

Benzene-*o*-bisthiaindoxyl.—See B., 1940, 726.

Synthesis of emetine and its analogues. Oxidation of 3-carbalkyloxy-1- β -phenylethylpyridinium salt [bromide]. S. SUGASAWA, K. SAKURAI, and T. OKAYAMA (Proc. Imp. Acad. Tokyo, 1940, 16, 225—228).—3-Carbomethoxy-, decomp. 197° , 3-carboethoxy-, m.p. 193 — 194° , and 3-carboxylamido-1- β -phenylethylpyridinium bromide, m.p. 209° (all prepared by addition), are oxidised by alkaline $K_3Fe(CN)_6$ to 1- β -phenylethyl-2-pyridone-, m.p. 190 — 191° , reduced catalytically, or better by Na-Hg, to 2-piperidone-5-carboxylic acid (I), m.p. 140° . $Ph[CH_2]_2NH_2$ (II) and $CO_2Et \cdot CH(CHO) \cdot CH_2 \cdot CO_2Et$ at room temp. give a product which after catalytic reduction in EtOH yields (with spontaneous ring-closure) the Et ester, b.p. 170 — $180^\circ/4$ mm., of 1- β -phenylethyl-2-pyrrolidone-4-carboxylic acid, m.p. 192 — 193° . (II) and $CO_2Et \cdot CH(CHO) \cdot [CH_2]_2 \cdot CO_2Et$ similarly give the Et ester, an oil, of (I).

E. W. W.

Action of diazomethane on acid chlorides of the pyridine series. A. DORNOW (Ber., 1940, 73, [B], 185—188).—Nicotinyl chloride hydrochloride with CH_2N_2 in Et_2O , followed by HCl, gives, after heating with H_2O , 3-hydroxyacetylpyridine, m.p. 41 — 42° (picrate, m.p. 142 — 143°), which has a hyperæmic

action. The 3-diazoacetylpyridine, intermediately formed, with cold conc. HCl gives the hydrochloride, decomp. 245 — 250° (darkening from 200°), of 3-chloroacetylpyridine, m.p. 51 — 52° (picrate, m.p. 132°). With C_5H_5N in $PhNO_2$, this gives 1-(3'-pyridoylmethyl)pyridinium chloride, m.p. 129 — 130° [product, $C_{13}H_{11}O_2N_5$, m.p. ~ 125 — 130° (decomp.), with picryl chloride]. isoNicotinic acid with $SOCl_2$ gives the chloride hydrochloride, which with CH_2N_2 in Et_2O gives 4-diazoacetylpyridine, m.p. ($+0.5H_2O$) 35 — 36° (picrate, m.p. 244°), converted by conc. HCl into 4-chloroacetylpyridine, m.p. ($+MeOH$) 103° (decomp.), and by AcOH into 4-acetoxyacetylpyridine, m.p. 68 — 69° [picrate, m.p. 148° (decomp.)]. E. W. W.

Arylpyridines. IV. 3- and 4-Pyridyldiphenyls. I. M. HEILBRON, D. H. HEY, and A. LAMBERT (J.C.S., 1940, 1279—1284).—Diazotised 3- $C_6H_4Ph \cdot NH_2$ and C_5H_5N give a mixture of 3- α -, b.p. 75 — $85^\circ/0.002$ mm., and 3- γ -pyridyldiphenyl, m.p. 81 — 82° , separated by fractional crystallisation of the picrates, m.p. 169° (I) and 231° (II), respectively. Reduction ($SnCl_2$ -HCl) of α -3-nitrophenylpyridine gives the NH_2 -derivative, which with Ac_2O affords the 3- α -NHAc-compound, m.p. 141 — 142° , converted through the NO-derivative (NOCl) and treatment with $C_6H_5(NO_2)_3 \cdot OH$ into (I). A similar series of reactions leads to β -3-amino-, m.p. 77 — 78° , and -acetamido-phenylpyridine, m.p. 135 — 136° , and 3- β -pyridyldiphenyl, b.p. 75 — $85^\circ/0.002$ mm. (picrate, m.p. 178 — 179°), and γ -3-amino-, m.p. 165 — 166° , and -acetamido-phenylpyridine, m.p. 171 — 172° , and (II). Diazotised 4- $C_6H_4Ph \cdot NH_2$ and C_5H_5N yield a mixture of 4- γ -, m.p. 215° and 4- α -pyridyldiphenyl picrates, m.p. 186 — 187° , the identity of which is similarly proved by the prep. of α -4-acetamido-, m.p. 135 — 136° , and -nitrosoacetamido-phenylpyridine, m.p. 88 — 89° (decomp.), 4- α -pyridyldiphenyl (III), m.p. 141 — 142° , β -4-acetamidophenylpyridine, m.p. 181 — 182° , 4- β -pyridyldiphenyl (IV), m.p. 151 — 152° (picrate, m.p. 208 — 210°), γ -4-acetamidophenylpyridine, m.p. 210 — 211° , and 4- γ -pyridyldiphenyl (V), m.p. 209° . Nitration (HNO_3 -AcOH) of (III) gives a mixture of 4'-nitro-, m.p. 213° (NH_2 -compound, m.p. 191 — 192° , and its Ac derivative, m.p. 236 — 237°), and 2'-nitro-4- α -pyridyldiphenyl, m.p. 136 — 137° [nitrate, m.p. 188 — 190° (decomp.)]; NH_2 -compound, m.p. 98 — 99° , and its Ac derivative, m.p. 146 — 147° . Similar nitration of (IV) affords 4'-, m.p. 192 — 193° , and 2'-nitro-4- β -pyridyldiphenyl, m.p. 124 — 125° , and of (V) yields 4'-, m.p. 196 — 197° , and 2'-nitro-4- γ -pyridyldiphenyl, m.p. 99 — 100° . The constitution of the nitration products is proved by oxidation to the corresponding $NO_2 \cdot C_6H_4 \cdot CO_2H$.

F. R. S.

Antiplasmodial action and chemical constitution. III. Carbinolamines derived from naphthalene and quinoline. H. KING and T. S. WORK. IV. Synthesis of complex carbinolamines and polyamines. T. S. WORK (J.C.S., 1940, 1307—1315, 1315—1320; cf. A., 1938, II, 163).—III. α -Naphthoyldiazomethane (from α - $C_{10}H_7 \cdot COCl$ and CH_2N_2 in Et_2O), m.p. 56° , with HCl in Et_2O gives α - $C_{10}H_7 \cdot CO \cdot CH_2Cl$, which when treated with the appropriate NHR_2 in Et_2O and reduced (H_2 , Pd-C, MeOH-aq. HCl) yields 1-naphthylidimethyl- (picrate,

m.p. 178—180°), -diethyl- (*picrate*, m.p. 136°), -di- β -hydroxyethyl- (*picrate*, m.p. 127—128°), and -di-*n*-propyl-amino- (*picrate*, m.p. 149—150°), and -piperidino-methylcarbinol (*hydrochloride*, m.p. 270°). 7-Methoxy-1-naphthacyl bromide (from $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$ as above; prep. starting from 1:7-CN \cdot C $_{10}$ H $_6$ ·SO $_3$ H described), b.p. 165—170°/1 mm.; similarly gives 7-methoxy-1-naphthylpiperidinomethylcarbinol (*hydrochloride*, m.p. 225—227°). 4-Quinolyl CH $_2$ Cl ketone, m.p. 101°, is prepared from the CHN $_2$ ketone, m.p. 83—84°. 4-Quinolyl CH $_2$ Br ketone hydrobromide [from Et 4-quinolylacetate (improved prep.)] similarly yields (as above) 4-quinolyl-diethyl- (*dipicrate*, m.p. 168°), -di-*n*-propyl- (*dipicrate*, m.p. 153°), and -di-*n*-amyl-amino- (*dipicrate*, m.p. 142°), -piperidino- [*dipicrate*, new m.p. 168° (decomp.); *hydrochloride*, m.p. 160°], and -4':4''-piperidylpiperidino-methylcarbinol [using *N*-benzoyl-4:4'-dipiperidyl (*hydrobromide*, m.p. 233°; *perchlorate*, m.p. 268°), obtained (together with the Bz $_2$ compound, m.p. 167°) from dipiperidyl and BzCl in COMe $_2$ -H $_2$ O at p_H 3-8] [tri-*hydrochloride*, m.p. >300° (decomp.); *tripicrate*, m.p. 195°]. 6-Methoxy-4-quinolyl CH $_2$ Br ketone hydrobromide similarly yields 6-methoxy-4-quinolyl-diethyl- (*dihydrochloride*, m.p. 182—183°), -di-*n*-butyl- (I) (*dihydrochloride*, m.p. 142°; *dipicrate*, m.p. 169°), -di-*n*-amyl- (II) (*dipicrate*, m.p. 155°), -di-isoamyl- (*dipicrate*, m.p. 156°), -di-*n*-hexyl- (III) (*dipicrate*, m.p. 173°), and -di-*n*-heptyl- (*dipicrate*; m.p. 130°), -piperidino- (*hydrochloride*, m.p. 164°), and -4':4''-piperidylpiperidino-methylcarbinol (*trihydrochloride*, anhyd. and +2H $_2$ O, decomp. >300°). 6-Methoxy-4-quinolylmethylcarbinol *hydrochloride*, m.p. 217°, was obtained in an attempt to prepare the NBut $_2$ -compound. Of these carbinolamines, (I), (II), and (III) show weak antiplasmodial activity (*P. relictum*) in canaries, the others none. Di-*n*-hexyl-, (IV), b.p. 122°/15 mm. (*tetrahydrate*, b.p. 114—116°/14 mm.; *hydrochloride*, m.p. 270°), and -heptylamine (V), m.p. 1° (lit. 30°) (*trihydrate*, m.p. 32—33°; *hydrochloride*, new m.p. 255°), are prepared by catalytic reduction (H $_2$, PtO $_2$, AcOH) of di-*n*-hexyl-, b.p. 185°/14 mm., and -heptyl-benzylamine, b.p. 205°/16 mm., respectively. *n*-Hexyl-, b.p. 146—148°/14 mm. (*hydrochloride*, m.p. 217—218°), and -heptyl-benzylamine (*hydrochloride*, m.p. 196°) are obtained as by-products in the prep. of (IV) and (V) from CH $_2$ Ph·NH $_2$ and the alkyl bromide.

IV. *p*-C $_6$ H $_4$ Ph·CO·CH $_2$ Cl with piperidine (I) in COMe $_2$ yields *p*-diphenyl piperidinomethyl ketone, m.p. 86° (*picrate*, m.p. 188°), reduced (H $_2$, PtO $_2$, EtOH-aq. HCl) to the corresponding carbinol, m.p. 120° [*hydrochloride*, m.p. 243° (decomp.); *methiodide*, m.p. 205°]. 4:4'-Di(chloroacetyl)diphenyl, m.p. 226—227° (from the acid chloride with CH $_2$ N $_2$ followed by HCl in C $_6$ H $_6$), with (I) in boiling CHCl $_3$ yields 4:4'-di(piperidinoacetyl)diphenyl, m.p. 140°, reduced (as above) to 4:4'-bis-(β -piperidino- α -hydroxyethyl)diphenyl, m.p. 158°. Sebacyl chloride with CH $_2$ N $_2$ in Et $_2$ O gives the bis(diazo-ketone), m.p. 91°, converted by HCl in C $_6$ H $_6$ into α -dichloro- β -diketododecane, m.p. 92°; this with (I) in COMe $_2$ yields the α -dipiperidino-derivative, m.p. 43°, reduced (as above) to α -dipiperidino- β -dihydroxydodecane, m.p. 78° (*dipicrate*, m.p. 152°), and with NHET $_2$ and similar

reduction yields α -bisdiethylamino- β -dihydroxydodecane (an oil) (*dipicrate*, m.p. 121°). [CH $_2$] $_{10}$ (COCl) $_2$ similarly yields the bis(diazo-ketone), m.p. 96°, α -dichloro-, m.p. 97°, and -dipiperidino- β -diketotetradecane (II), m.p. 48°, which is not reduced by H $_2$ -PtO $_2$, and with Al-Hg in neutral solution gives β -diketotetradecane, m.p. 75°, and a base from which no cryst. derivative could be obtained. MgPr $^+$ Br and (II) yield α -dipiperidino- β -dihydroxy- β -dipropyltetradecane, b.p. 230—240°/0.3 mm. NN'-Di-*p*-toluenesulphonylbenzidine (III) with NEt $_2$ ·[CH $_2$] $_3$ ·Cl (IV), new b.p. 75—76°/29 mm., in boiling aq. EtOH-NaOH gives a product hydrolysed by AcOH-conc. HCl at 180° under pressure to NN'-bis-(γ -diethylaminopropyl)benzidine, b.p. 230—250°/0.9 mm. [*tetrahydrobromide*, m.p. 260° (decomp.)]. NHBz·[CH $_2$] $_5$ ·Cl, (III), and NaOH in H $_2$ O-COMe $_2$ at 150—160° under pressure yield NN'-di-*p*-toluenesulphonyl-NN'-di- ϵ -benzamidoamylbenzidine, m.p. 192°, hydrolysed to NN'-di- ϵ -aminoamylbenzidine, m.p. 270° (decomp.) [*tetrahydrochloride* (hygroscopic)]. 4:4'- and 2:4'-Dipiperidyl with NEt $_2$ ·[CH $_2$] $_2$ ·Cl in EtOH at 100° under pressure yield 1:1'-bis- β -diethylaminoethyl-4:4'-, b.p. 200—230°/0.3 mm. [*tetrapicrate*, m.p. 250° (decomp.)], and -2:4'-dipiperidyl, b.p. 205—210°/0.5 mm. (*tetrapicrate*, m.p. 170°). Tetrahydroquinoline with (IV) at 100° under pressure yields 1- γ -diethylaminopropyltetrahydroquinoline, b.p. 192°/10 mm. (*dipicrate*, m.p. 147°). α -Di-*p*-toluenesulphonamido-hexane, m.p. 152° (from NH $_2$ ·[CH $_2$] $_6$ ·NH $_2$, *p*-C $_6$ H $_4$ Me·SO $_2$ Cl, and aq. NaOH), with (IV) in aq. EtOH-NaOH at 100° gives a product hydrolysed (AcOH-HCl at 180°) to α -di-(γ -diethylaminopropylamino)hexane, b.p. 135—140°/0.5 mm. (*tetrahydrobromide*, m.p. 64°). α -Di-*p*-toluenesulphonamido-dodecane (V), m.p. 129°, similarly yields α -di-(γ -diethylaminopropylamino)dodecane, b.p. 178—184°/1.5 mm. [crude hydrobromide (hygroscopic), m.p. 142—143°]. iso-C $_5$ H $_{11}$ Br and (V) under similar conditions give α -di-isoamylaminododecane (*dihydrochloride*, m.p. 318°). None of the compounds described has antiplasmodial activity, thus showing the importance of the quinoline nucleus.

A. LI.

Nitrogen compounds in petroleum distillates. XVIII. Isolation, ozonisation, and synthesis of 2:4-dimethyl-8-sec-butylquinoline. L. M. SCHENCK and J. R. BAILEY (J. Amer. Chem. Soc., 1940, 62, 1967—1969; cf. A., 1940, II, 24).—Cumulative, followed by countercurrent, extraction of the residual bases from 2:3:4-trimethyl-8-ethyl- and -8-*n*-propyl-quinoline (I) (A., 1933, 1305) gives a further amount of (I) and 2:4-dimethyl-8-sec-butylquinoline (II), b.p. 310° (*picrate*, m.p. 148—150°). K $_2$ Cr $_2$ O $_7$ -dil. H $_2$ SO $_4$ oxidises (II) to 2:4-dimethylquinoline-8-carboxylic acid. Ozonisation of (II) in CCl $_4$ and oxidation of the product by H $_2$ O $_2$ gives CHMeEt·CO $_2$ H (III). 70% of (II) is obtained from CH $_2$ Ac $_2$ and *o*-CHMeEt·C $_6$ H $_4$ ·NH $_2$. CH $_2$ Ac $_2$ and *p*-CHMeEt·C $_6$ H $_4$ ·NH $_2$ give 2:4-dimethyl-6-sec-butylquinoline, b.p. 321° (*picrate*, m.p. 141—142°), giving (III) by H $_2$ O $_2$ and then H $_2$ O $_2$. Successive treatment with O $_3$, 3% H $_2$ O $_2$, and boiling aq. K $_2$ CO $_3$ converts (I) into NH $_3$, H $_2$ C $_2$ O $_4$, HCO $_2$ H, AcOH, Pr $^+$ CO $_2$ H, and a little CO $_2$.

R. S. C.

Carbazolecarboxyl chlorides.—See B., 1940, 762.

Sulphanilamides. I. 3-(p-Aminobenzenesulphonamido)carbazole. A. NOVELLI (Anal. Assoc. Quím. Argentina, 1940, 28, 87—90).—3-Aminocarbazole (modified prep.) with *p*-NHAc·C₆H₄·SO₂Cl in COMe₂ boiled in presence of C₂H₅N yields the *Ac* derivative, m.p. 252—255°, of 3-(*p*-aminobenzenesulphonamido)carbazole, m.p. 256—257°. F. R. G.

Effect of *p_H* and irradiation on the ultra-violet absorption spectrum of barbituric acid.—See A., 1940, I, 402.

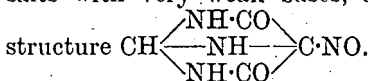
Barbituric acids.—See B., 1940, 702

Synthesis of tetrahydropyrimidines. S. R. ASPINALL (J. Amer. Chem. Soc., 1940, 62, 2160—2162).—NH₂·[CH₂]₃·NH₂ and EtOAc (1 : 3 mol.) at 165° give 60% of the *Ac*₁ derivative (I), b.p. 130°/3 mm. (*picrate*, m.p. 197°), which with CaO at 250° gives 90% of 2-methyl-3 : 4 : 5 : 6-tetrahydropyrimidine (II), b.p. 91°/4 mm., m.p. 75° (lit., 72—74°) [*phenylcarbamido*-derivative, m.p. 147°; *picrate*, m.p. 157° (lit., 152°)]. Acetylation at 150° (or 250°) gives a mixture of (I) and (II), but dehydration of this crude product gives 70% of (II). NHBz·[CH₂]₃·NH₂ (*phenylcarbamido*-derivative, m.p. 166° and 2-phenyl-3 : 4 : 5 : 6-tetrahydropyrimidine, m.p. 87° (lit., 72—78°), b.p. 155—165°/5 mm. (*picrate*, m.p. 181°), are similarly obtained. R. S. C.

Attempts to find new antimalarials. XVII. Derivatives of 5 : 6 : 3' : 2'-pyridoquinoline. W. O. KERMACK and (MISS) A. P. WEATHERHEAD (J.C.S., 1940, 1164—1169).—2-Hydroxy-4-methyl-5 : 6 : 3' : 2'-pyridoquinoline, m.p. 330°, prepared from 6-amino-2-hydroxy-4-methylquinoline (Skraup reaction), with PCl₅ gives the 2-*Cl*-compound, m.p. 204°, which with the appropriate reagent affords 2-piperidino-, m.p. 104° (*hydrobromide*, m.p. >400°), 2-piperazino-(+2H₂O), m.p. 110°, anhyd., m.p. 125°, 2-β-diethylaminoethylamino-, m.p. 123° (*hydrobromide*, m.p. 229°), and 2-γ-diethylaminopropylamino-4-methyl-5 : 6 : 3' : 2'-pyridoquinoline *hydrobromide* (+2H₂O), m.p. 265°. 2-Chloro-6-nitro-4-methylquinoline and NEt₂·[CH₂]₂·NH₂ yield 6-nitro-2-β-diethylaminoethylamino-4-methylquinoline *hydrochloride*, m.p. 165°, and *picrate*, m.p. 210°. 4-Hydroxy-2-methyl-5 : 6 : 3' : 2'-pyridoquinoline, m.p. 358°, obtained from 6-amino-4-hydroxy-2-methylquinoline, in a similar series of reactions, leads to 4-chloro-, m.p. 149°, 4-piperidino-, m.p. 163° (*picrate*, m.p. 225°), and 4-β-diethylaminoethylamino-2-methyl-5 : 6 : 3' : 2'-pyridoquinoline (+H₂O), m.p. 68°. *p*-NH₂·C₆H₄·NHAc and Et oxaloacetate condense to Et α-*p*-acetamidooxalinofumarate, m.p. 122°, cyclised to Et 6-acetamido-4-hydroxyquinoline-2-carboxylate, m.p. 309°, which is hydrolysed (HCl) to 6-amino-4-hydroxyquinoline-2-carboxylic acid (I), m.p. 308° (*hydrochloride*, m.p. >400°). NH₂Ph and Et oxaloacetate give Et 4-hydroxyquinoline-2-carboxylate, m.p. 212°, which is nitrated (H₂SO₄—HNO₃) to the 6-NO₂-compound, m.p. 286°; reduction of this with SnCl₂—HCl affords (I). The sulphate, m.p. 275°, of 6-amino-4-hydroxyquinoline (*dihydrochloride*, m.p. 305°) gives (Skraup reaction) 4-hydroxy-5 : 6 : 3' : 2'-pyridoquinoline (II) (+0.5H₂O), m.p. 298°, which is

converted successively into the 4-*Cl*-, m.p. 147°, 4-β-diethylaminoethylamino-, m.p. 235°, and 4-γ-diethylaminopropylamino-compounds (*picrate*, m.p. 231°). (II) has the angular structure. F. R. S.

Colour in relation to chemical constitution of the organic and inorganic salts of oximinomalonylguanidine. I. N. D. DASS and S. DUTT (Proc. Nat. Acad. Sci. India, 1939, 9, 93—98).—Oximinomalonylguanidine (I) [from guanidine carbonate with CH₂(CO₂Et)₂ at 150—160°, followed by HNO₂] in H₂O is violet and has an absorption spectrum almost identical with those of its *K*, *Na*, NH₄, NH₃Me, NH₃Et, NH₂Me₂, NH₂Et₂, NHMe₃, NH₃Pr, NH₃Bu, and piperidinium salts. (I) does not form salts with very weak bases, and probably has the



A. LI.

Phthalocyanines and related compounds. XVII. Intermediates for the preparation of tetrabenzoporphins : acids derived from phthalimidine. R. P. LINSTAD and G. A. ROWE. XVIII. Intermediates for the preparation of tetrabenzoporphins : Thorpe reaction with phthalonitrile. P. A. BARRETT, R. P. LINSTAD, and (in part) J. J. LEAVITT and G. A. ROWE. XIX. Tetrabenzoporphin, tetrabenzmonozaporphin, and their metallic derivatives. P. A. BARRETT, R. P. LINSTAD, F. G. RUNDALL, and G. A. P. TUEY (J.C.S., 1940, 1070—1076, 1076—1079, 1079—1092).—XVII. Condensation of iminophthalimidine with CH₂Ac·CO₂Et at 140° (no catalyst) gives *Et phthalimidyl-3-acetoacetate*, m.p. 101°, with evolution of heat and NH₃; with CH₂(CO₂Et)₂, a smaller yield (at 199°) of 3-dicarb-ethoxymethylenephthalimidine (I), m.p. 104—105°, is obtained. Both products are readily oxidised (KMnO₄) to phthalimide. Hydrolysis [Ba(OH)₂] of (I) affords 3-carboxymethylenephthalimidine (II), m.p. 220° (*Me ester*, m.p. 124—125°). This acid is also obtained from phthalylacetic acid and aq. NH₃ after acidification at room temp. but if acidified at 0—5°, the monohydrate of *o*-carbamybenzoylacetic acid (III), m.p. 120° (*Me ester*, m.p. 116—117°), is formed; this is identical with the “dihydrate” of (II). Reduction of (II) with Na—Hg gives 3-carboxymethylphthalimidine (*Me ester*, m.p. 139—140°), identical with isoindolinone-3-acetic acid. This substance is also formed by reduction (Na—Hg) of (III) at room temp. but at 0°, β-hydroxy-β-*o*-carbamyphenylpropionic acid, m.p. 180°, is obtained; this, when heated under reduced pressure at 105°, yields the phthalimidine. *o*-CN·C₆H₄·[CH₂]₂·CO₂H (*Me ester*, b.p. 290—295°) is prepared by reduction (Na—Hg) of the corresponding cinnamic acid.

XVIII. Condensation (Thorpe reaction) of *o*-C₆H₄(CN)₂ with CH₂Ph·CO·CN gives 1-amino-3-cyanobenzylidenephthalimidine, m.p. 207—209°, isolated as the *hydrochloride*, m.p. 299°, and hydrolysed (HCl—EtOH) to 3-cyanobenzylidenephthalimidine, m.p. 228—230°. Similar condensation with *o*-CN·CH₂·CO₂Et affords 3-cyanocarbethoxymethylenephthalimidine, m.p. 170°, and with CH₂(CO₂Et)₂ yields 1-imino-3-dicarb-ethoxymethylenephthalimidine, m.p. 97° (*hydrochloride*, m.p. 210°). Hydrolysis of this acid with NaOH—

EtOH leads to the *imino-acid* (IV), m.p. 280—300° (decomp.); with HCl-H₂O, 3-*dicarbethoxymethylphthalimidine*, m.p. 108°, is obtained, which is hydrolysed to (II).

XIX. Zn and (IV) when heated at 330—340° and treated with HCl give *tetrabenzmonazaporphin*, green crystals with a bluish-purple lustre, which forms Cu, Fe^{II}, and Mg derivatives; its structure is proved by quant. oxidation. The substance is also produced from MgMeI and *o*-C₆H₄(CN)₂ (17% yield). 3-Amino-1:1-dimethyl-*ψ*-isoindole and Ac₂O yield 2-*acetyl-3:3-dimethylphthalimidine*, m.p. 105—106°, hydrolysed to 3:3-*dimethylphthalimidine*, m.p. 162°, which gives only a trace of pigment with Zn(OAc)₂. 3-Carboxymethylphthalimidine and Zn afford Zn *tetrabenzporphin*, converted by HCl into *tetrabenzporphin* (Mg derivative), of which the structure is proved by quant. oxidation. *o*-CN·C₆H₄·COMe may be used for the prep. of Cu derivatives of *tetrabenz-monaza*-, *-diaz*-, and *-triaz*a-porphin. The absorption spectra of all these compounds have been measured quantitatively and the results are compared with those for the analogous phthalocyanine and *tetrabenztriazaporphin* derivatives. The various methods available for their prep. are reviewed and possible mechanisms are discussed.

F. R. S.

Phthalocyanines.—See B., 1940, 660.

Preparation of biliverdin. R. LEMBERG and J. W. LEGGE (Austral. J. Exp. Biol., 1940, 18, 95—98).—The "blue stable stage" in the oxidation of bilirubin by H₂O₂ in acid-EtOH solution (method of Malloy and Evelyn) is biliverdin (I) (dehydrobilirubin). A new method for the prep. of (I) based on this yields about 40% of pure cryst. product. Prolonged oxidation by H₂O₂ attacks the unsaturated side-chains of (I) but not the tetrapyrrole nucleus; there are no marked changes in the absorption spectrum.

D. M. N.

Cyanine dyes.—See B., 1940, 703.

Electron-sharing ability of organic radicals.

XI. 2-Thienyl- and 2-mesityl-pyrrolidines. J. G. KRECHNER and I. B. JOHNS (J. Amer. Chem. Soc., 1940, 62, 2183—2184).—Mg 2-thienyl iodide and Cl·(CH₃)₂·CN in boiling Et₂O and then in xylene give 2-2'-*thienylpyrroline* (27.5%), m.p. 57°, b.p. 111.1—112.1°/4 mm. (picrate, m.p. 197.7°), reduced by Sn-HCl (Na-EtOH causes decomp.) to 2-2'-*thienylpyrrolidine* (I), b.p. 88—89°/3 mm., -log *K*_B 6.47 in MeOH, 4.65 in H₂O (picrate, m.p. 187.6°). 1:3:5:2-C₆H₂Me₃Br gives similarly 2-*mesitylpyrroline*, b.p. 101—102° (corr.)/2 mm. [picrate, m.p. 180° (corr.)], and *-pyrrolidine*, b.p. 124.2° (corr.)/3.5 mm., -log *K*_B 6.73 in MeOH (picrate, m.p. 194.6°; resists resolution). (I) gives a camphorate, m.p. 128—129°, [α]_D²⁵ +15.54° in EtOH, and thence a partly resolved base, [α]_D²⁵ -3.12° in EtOH.

R. S. C.

Chemotherapy. I. Substituted sulphanilamidopyridines. R. O. ROBLIN, jun., and P. S. WINNEK. II. **Heterocyclic sulphanilamido-compounds.** R. O. ROBLIN, jun., J. H. WILLIAMS, P. S. WINNEK, and J. P. ENGLISH (J. Amer. Chem. Soc., 1940, 62, 1999—2002, 2002—2005).—Products marked (A) below are more active chemotherapeutic

ally than sulphanilamide and sulphapyridine; those marked (S) are slightly active; others are inactive. Solubility in H₂O and max. blood levels are recorded. The importance of the latter as indicating presence in the blood of a reasonable amount of the drug is stressed. M.p. are corr.

I. The following are prepared. 2- (A), m.p. 190—191°, and 3-sulphanilamidopyridine (A), m.p. 258—259° (decomp.); 2-*chloro*- (A), m.p. 186—187°, 2-*bromo*- (A), m.p. 196—197°, 2-*amino*-, m.p. 207—208°, 2-*hydroxy*-, m.p. 243—244° (decomp.), and 2-*ethoxy*-, m.p. 207—208°, 5-*sulphanilamidopyridine*; 5-*bromo*-, m.p. 199—200°, 5-*iodo*-, m.p. 220—221°, 5-*nitro*- (A), m.p. 220—221°, 5-*amino*- (A), m.p. 157—158°, and 3-*ethoxy*- (S), m.p. 198—200°, 2-*sulphanilamidopyridine*; 2:5-*disulphanilamidopyridine* (S), m.p. 215—216°. The effect of substituents is remarkable. Hydrogenation [Pd(OH)₂-CaCO₃] of 2-*p*-nitrobenzenesulphonamido-3-ethoxypyridine in 95% EtOH at 50°/3—4 atm. gives 2-*p*-*hydroxylaminobenzenesulphonamido*-3-ethoxypyridine, m.p. 189—190°.

II. Addition of malic acid and then of NH₄C(NH₂)₂·H₂SO₄·0.5H₂O to 20% fuming H₂SO₄ at 0° gives *isocytosine sulphate* (69%), converted by boiling POCl₃ into 4-*chloro*-2-aminopyrimidine (71%), which was H₂-Pd(OH)₂-CaCO₃ in MeOH or EtOH at 50°/3—4 atm. gives 2-aminopyrimidine. By the usual methods are obtained: 2-*sulphanilamido-thiazole* (A), m.p. 201—202°, 4-*methylthiazole* (A), m.p. 237—238°, *-benzthiazole*, m.p. 304—305° (decomp.), 4-*p*-*diphenylthiazole*, m.p. 216—217°, 1:3:4-*thiadiazole*, *p*-NH₂·C₆H₄·SO₂·NH·C<S<CH<N<N<, m.p. 216—218° (decomp.), *-pyrimidine* (I) (A), m.p. 255—256° (decomp.) (Na salt; N⁴-Ac derivative, m.p. 258—259°), and 4-*methylpyrimidine* (II) (A), m.p. 235—236° (decomp.) (N⁴-Ac derivative, m.p. 248—249°); 1-*sulphanilyl*-3-*methyl*- (S), m.p. 166—167°, and 4-*sulphanilamido*-1-*phenyl*-2:3-*dimethyl*-, m.p. 260—261° (decomp.), 5-*pyrazolone*; 5-*p*-nitrobenzenesulphanilamidotetrazole (III), m.p. 185—186° (decomp.); *sulphanilylguanidine* (IV) (S), m.p. 189—190° (decomp.); 5-*sulphanilamidouracil*, m.p. 277—279° (decomp.). Attempts to reduce the NO₂ of (III) led to (IV) or its NO₂-derivative. (I) and (II) show promise clinically. To avoid confusion it is proposed to call (I), (II), etc. "sulphadiazines." R. S. C.

Synthesis of ωω'-bis-2'-amino-4'-thiazolyl-alkanes and N⁴-2'-thiazolylsulphanilamides. J. WALKER (J.C.S., 1940, 1304—1307).—Adipoyl chloride and CH₂N₂ give αδ-*bis-diazo*-, m.p. 69—71°, converted by HCl into the *-chloroacetyl-n-butane*, m.p. 81—82°, which with CS(NH₂)₂ yields αδ-*bis-2-aminoyl-4-thiazol-n-butane*, m.p. 220—221° [dihydrochloride, m.p. 284—285° (efferv.)]. Similarly αζ-*bischloroacetyl-n-hexane*, m.p. 85—86°, prepared from suberoyl chloride, with CS(NH₂)₂ forms αζ-*bis-2-amino-4-thiazolyl-n-hexane*, m.p. 204—205° (dihydrochloride, m.p. 308—310°). αθ-*Bis-2-amino-4-thiazolyl-n-octane*, m.p. 180—181° [dihydrochloride, m.p. 309—311° (efferv.)], and ακ-*bis-2-amino-4-thiazolyl-n-decane*, m.p. 168—171° (dihydrochloride, m.p. 274—276°), are similarly obtained. The Arndt-

Eistert method has been applied to the bis-homologation of sebacic and adipic acids. 4-Sulphonamidophenylthiocarbamide, m.p. 209°, prepared from sulph-anilamide and NH_4CNS , condenses with $\text{CH}_2\text{Cl}\cdot\text{COMe}$ and $\text{COMe}\cdot\text{CHBr}\cdot[\text{CH}_2]_2\cdot\text{OAc}$ to give respectively N^4 -4'-methyl-, m.p. 234—235°, and N^4 -5'- β -hydroxyethyl-4'-methyl-2'-thiazolylsulphanilamide, m.p. 211—212°.

F. R. S.

Anthraquinonylthiazoles.—See B., 1940, 727.

Minor alkaloids of *Duboisia myoporoides*. III. Valeroidine. W. F. MARTIN and W. MITCHELL (J.C.S., 1940, 1155—1157).—Valeroidine (I) and Ac_2O give the Ac derivative, isolated as the hydrobromide, m.p. 197°, and with Bu^iCOCl , diisovaleryl-dihydroxytropan hydrobromide, m.p. 176—177°, is obtained. Dihydroxytropan also forms a Ac_2 derivative, isolated as the hydrobromide, m.p. 219—220°. The hydrobromide of (I) is demethylated by SOCl_2 to norvaleroidine hydrobromide, m.p. 270°, $[\alpha]_D^{20} +1.0^\circ$ in H_2O . Attempts to orient the OH groups have given obscure results.

F. R. S.

Synthesis of formylphenacetiltropeine. Y. ASAHINA and H. NOGAMI (Proc. Imp. Acad. Tokyo, 1940, 16, 229—230).—Homotropine hydrochloride with $\text{NaOAc}\cdot\text{Ac}_2\text{O}$ gives acetylhomotropine, an oil [picrate, m.p. 229° (decomp.)], the hydrochloride, m.p. 67°, of which is catalytically reduced in EtOH (Pd-C) (cf. Rosenmund *et al.*, A., 1928, 1005) to phenacetiltropeine, an oil (picrate, m.p. 169°). This with $\text{HCO}_2\text{Et}\cdot\text{Na}\cdot\text{Et}_2\text{O}$, followed by H_2O , gives formylphenacetiltropeine ("atropanal") (I), m.p. 214° (decomp.) [hydrochloride, m.p. 204° (decomp.); oxime, m.p. 139° (decomp.) (hydrochloride, m.p. ~165°)]. This has no mydriatic action, and is weaker than atropine (II) in its paralyzing action on parasympathetic endings, but is a strong respiratory stimulant causing small rise of blood pressure. It is suggested that (II) injected into the portal vein is (at least partly) oxidised to (I) in the liver.

E. W. W.

Gelsemine. I. Reduction of gelsemine. T. T. CHU and T. Q. CHOU (J. Amer. Chem. Soc., 1940, 62, 1955—1957).—Gelsemine (I) absorbs 2 H in presence of PtO_2 in MeOH, giving dihydrogelsemine, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$, + COMe_2 , m.p. 224—225°, $[\alpha]_D^{17} +78.5^\circ$ in CHCl_3 [hydrochloride, m.p. 318—320° (decomp.); hydrobromide, m.p. 328—330° (decomp.); hydriodide, m.p. 294—295°; nitrate, m.p. 285° (decomp.); methiodide, m.p. 301—302° (decomp.)]. Zn-HCl in presence of a little PtCl_4 or PdCl_2 isomerises (I) to isogelsemine, + COMe_2 , froths at 105°, resolidifies, melts at 198—202°, or solvent-free at 200—202°, $[\alpha]_D^{19} +38.8^\circ$ [methiodide, m.p. 279—280° (decomp.)], and gives also a small amount of a substance, $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}$, sinters at 261°, decomp. 265—267°, $[\alpha]_D^{18} -14.9^\circ$ in MeOH [hydrobromide, m.p. 305—308° (decomp.); methiodide, decomp. 262—265°].

R. S. C.

Alkaloids of fumariaceous plants. XXIX. Constitution of cryptocavine. R. H. F. MANSKE and L. MARION (J. Amer. Chem. Soc., 1940, 62, 2042—2044).—Cryptocavine methosulphate and $\text{Na}\cdot\text{Hg}$ in hot dil. H_2SO_4 give tetrahydromethylcryptocavine, converted by AcCl into anhydrotetrahydro-

methyl-cryptocavine (-cryptopine), m.p. 111°, which with $\text{KMnO}_4\cdot\text{COMe}_2$ gives 5:6:2:1- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Me}\cdot\text{CHO}$ and 4:5:1:2- $(\text{OMe})_2\text{C}_6\text{H}_2(\text{CHO})\cdot[\text{CH}_2]_2\cdot\text{NMe}_2$. Cryptocavine is thus cryptopine (J.C.S., 1916, 109, 815) in which the positions of the CO and CH_2 are reversed. R. S. C.

Sulphophenylarsinic acids and their derivatives. III. *p*-Sulpho- and *p*-sulphonamidodiphenylarsinic acids. J. F. ONETO and E. L. WAY (J. Amer. Chem. Soc., 1940, 62, 2157—2158).—The Bart reaction in EtOH, applied to $\text{p-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (I) and AsPhCl_2 , gives (I) (64%) and PhAsO_3H_2 (84%), but diazotisation of (I) in H_2O , addition of AsPhCl_2 in EtOH and then of a little CuBr, and finally heating at 80° gives phenyl-*p*-sulphophenylarsinic acid. Addition of AsPhO , NaOH, and a little CuSO_4 in H_2O to diazotised sulphanilamide gives 11% of phenyl-*p*-sulphonamidophenylarsinic acid (II), m.p. 229—231°, obtained in 23 and 28—30% yields by the Sakellarios and Scheller methods, respectively. $\text{NaNO}_2\cdot\text{H}_2\text{SO}_4\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ converts AsPhCl_2 into PhAsO_3H_2 (86%). $\text{HCl}\cdot\text{HI}\cdot\text{SO}_2$ converts (II) into phenyl-*p*-sulphonamidophenylchloroarsine, m.p. 106—107°. The bromoarsine, m.p. 100—101°, similarly obtained, with aq. NH_3 at 100° gives diphenyldi-*p*-sulphonamidophenylarsyl oxide. $\text{HI}\cdot\text{AcOH}$ converts (II) into the iodoarsine, m.p. 121—122°, and NaOCl gives phenyl-*p*-sulphonchloroamidophenylarsinic acid, m.p. 160—161°. R. S. C.

Colour tests for organo-lithium compounds. H. GILMAN and J. SWISS (J. Amer. Chem. Soc., 1940, 62, 1847—1849).—(a) When a solution of LiAlk is treated successively with $\text{p-C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2\cdot\text{C}_6\text{H}_6$, $\text{COPh}_2\cdot\text{C}_6\text{H}_6$, H_2O , and HCl, a red colour develops in the aq. layer owing to the reactions: $\text{LiAlk} + \text{p-C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2$ (I) \rightarrow $\text{Li}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{p}$ (II) + AlkBr ; (II) + $\text{COPh}_2 \rightarrow (\text{HCl}) \text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{Cl}$. LiAr does not react. MgRHal does not react with (I) and with COPh_2 gives colourless $\text{CPh}_2\cdot\text{R}\cdot\text{OH}$. LiMe and $\text{LiC}\cdot\text{CR}$ do not react. (b) When LiR is added to CHPh_3 in C_6H_6 or Et_2O , a yellow colour develops in 0.5—2 min., but Grignard reagents do not react. R may be alkyl or aryl. LiMe and Li 4-dibenzfuryl give no colour. For LiBu^a the limit is 0.02—0.03M. R. S. C.

Hydrogen bond in protein structure.—See A., 1940, I, 404.

Hydrogen bridge models for globular proteins.—See A., 1940, I, 404.

[Apparatus for] micro-analysis of gases.—See A., 1940, I, 420.

Micro-Kjeldahl apparatus.—See A., 1940, I, 421.

Identification of alcohols by means of optical properties of esters of carbanilic acid. B. T. DEWEY and N. F. WITT (Ind. Eng. Chem. [Anal.] 1940, 12, 459—460).—The phenylurethanes of *n*-alcohols $\text{C}_1\text{—C}_{12}$, and of $\text{CH}_2\text{Ph}\cdot\text{OH}$, $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{OH}$, and $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{OH}$ have been prepared and their m.p. and optical crystallographic data recorded. The optical properties provide a means of identifying the urethanes even when they are mixed with $\text{CO}(\text{NHPh})_2$. J. D. R.

A., II.—Organic Chemistry

DECEMBER, 1940.

Preparation and properties of aliphatic hydrocarbons. L. SCHMERLING, B. S. FRIEDMAN, and V. N. IPATIEV (J. Amer. Chem. Soc., 1940, 62, 2246—2249).—Hydrogenations below are effected in presence of Ni-kieselguhr at 100 kg. per sq. cm.

COMe·CH·CMe₂ and H₂ at 150° give CHMeBu^β·OH (70%), b.p. 128—131° (with 28% of COMeBu^β, b.p. 115—117°), dehydrated by Al₂O₃ (activated in this and other cases) at 427° to β-methylpentenes, b.p. 55—56°, which with H₂ at 50° give CHMe₂Pr^α, b.p. 59.4—59.6°/750 mm., octane no. 71.5. Hydrogenation of COMe·CH₂·CMe₂·OH gives OH·CHMe·CH₂·CMe₂·OH (II), b.p. 194—195°, with much Pr^βOH. With Al₂O₃ at 427°, (I) gives, by way of the epoxy-compound, much MeCHO and CMe₂·CH₂ with some COMe₂ and CHMe·CH₂. With H₂-Cu-Ni at 200°, (I) gives only Pr^βOH. Hydrogenation of COMeBu^γ at 200° gives CHMeBu^γ·OH (100%); CHMeBu^γ·OAc at 450° gives 90% of CHBu^γ·CH₂, b.p. 41—42°, hydrogenated in presence of Ni-Cu (not other catalysts) at 250° to a mixture of Pr^β₂ (85%), b.p. 57.4—57.5°/745 mm., octane no. 94, and EtBu^γ, b.p. 49.4—49.5°/753 mm., octane no. 93. (CMe₂·OH)₂ and Al₂O₃ at 427° give 55—70% of (CH₂·CMe)₂, b.p. 68—70° (with 25—30% of COMeBu^γ), which with H₂ gives Pr^β₂, also obtained from COMeBu^γ by way of CHMeBu^γ·OH and (H₂C₂O₄; 110—120°) CMePr^β·CH₂ + (CMe₂)₂. Hydrogenation (Ni-kieselguhr or Ni-Cu) of CHMeBu^γ·OH gives mixtures. COMeBu^γ and MgMeBr give 85% of CMe₂Bu^γ·OH, b.p. 128—129°, and thence (Al₂O₃-NiO; H₂; 250—260°/100 kg. per sq. cm.) Pr^βBu^γ, b.p. 80.5—81°/748 mm., octane no. 100. Similarly, (CMeEt·OH)₂ (prep. from COMeEt and Mg), b.p. 94—95°/10 mm., gives (CHMeEt)₂, b.p. 118—118.3°/750 mm., octane no. 84.5, and CHMeEtBu^γ, b.p. 110—110.5°/749 mm., octane no. 100. With Al₂O₃ at 325°, (II) gives CMe₂·CMePr^β, b.p. 114.5—114.9°/749.5 mm., and thence CHMePr^β₂, b.p. 112.3—112.4°/736 mm., octane no. 94.5. R. S. C.

High-temperature chlorination of paraffin hydrocarbons. W. E. VAUGHAN and F. F. RUST (J. Org. Chem., 1940, 5, 449—471).—Mixtures of C₂H₆, C₂H₄, C₃H₈, EtCl, Pr^αCl, Pr^βCl, or EtBr with Cl₂ diluted with CO₂ or N₂ are freed from O₂ by CrSO₄ or CrCl₂ and passed through heated tubes in the absence of light. The effluent mixtures are analysed by titration or by distillation. In the chlorination of C₂H₆ at moderate temp. reaction is expressed $d[\text{HCl}]/dt = k[\text{Cl}_2][\text{C}_2\text{H}_6]$ and the scheme $\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$, $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$, $\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{EtCl} + \text{Cl}$; $\text{Cl} + \text{W} \rightarrow \text{chain ending}$. The chain nature of the reaction is further demonstrated by the inhibiting action of O₂. At or near the temp. at which un-

controllable reaction would occur in the absence of O₂ production of HCl occurs according to $d[\text{HCl}]/dt = k[\text{Cl}]^{1/2}[\text{C}_2\text{H}_6]^{3/2}/[\text{O}_2]$. Chlorination of C₂H₆ is highly dependent on the surface, which appears to produce Cl atoms and to terminate chains. Chlorination of C₃H₈ is very similar to that of C₂H₆. At ~250° approx. equal proportions of Pr^αCl and Pr^βCl are formed. Pr^αCl gives all three chlorides, the *sec.* H atoms being very reactive despite their smaller no. Pr^βCl is less reactive than Pr^αCl probably because it has only one *sec.* H. EtCl is less reactive than C₂H₆. Large proportions of C₂H₄ are obtained at >280°; at 415° in absence of halogen but under otherwise comparable conditions EtCl scarcely yields C₂H₄ and HCl. The principal product is probably a consequence of a radical chain, $\text{Cl} + \text{EtCl} \rightarrow \text{HCl} + \text{C}_2\text{H}_4\text{Cl}$; $\text{C}_2\text{H}_4\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{Cl}$. Small amounts of O₂ suppress the action almost completely whilst at higher temp. some change occurs. CH₂·CHCl, unsaturated dichloride, CHMeCl₂, CMeCl₃, and (CH₂Cl)₂ are also formed. EtBr at 278° affords EtCl, EtBr, C₂H₄, and a little C₂H₄ClBr. In mixtures of C₂H₆ and C₂H₄ the former is dominantly or almost exclusively the reactive component. The production of CH₂·CH·CH₂Cl from CH₂·CHMe is thus explained. Chlorination of C₂H₆, C₃H₈, and cyclopentane in the gas phase and of *n*-C₅H₁₂ in the liquid phase is accelerated by PbEt₄. C₂Ph₆ is a useful catalyst in the liquid phase whilst CH₂N₂ is somewhat less effective than PbEt₄ in the gaseous state. H. W.

High-temperature chlorination of olefine hydrocarbons. F. F. RUST and W. E. VAUGHAN (J. Org. Chem., 1940, 5, 472—503).—Dynamic studies of the interaction of C₂H₄ and Cl₂ can be made only in presence of a diluent (N₂). At 308° the total amount of addition is \gg that of substitution whereas at 346° the substitutive steps are dominant. The mol. % of tri- and tetra-chlorides are relatively const. and the principal variations are in the amounts of unsaturated and simple additive products. The formation of higher chlorides from CH₂·CHCl is important in this connexion. At 485° there is extensive decomp. accompanied by formation of C₂H₂ undoubtedly by elimination of HCl from CH₂·CHCl. A simple relationship between rate of reaction and concn. of reactants could not be adduced. At low temp., where only addition occurs, increased surface causes an increase in the amount of reaction, probably as a result of catalysed bimol. association as well as initiation of chains. Glass wool is particularly effective. At higher temp. surface suppresses reaction, probably as a consequence of the termination of chains initiated in the gas phase. The chains

involve both addition and substitution at these temp. Controlled inhibition by O_2 does not persist to so high a temp. with olefines as with paraffins. The chain character of the gas-phase addition and substitution of olefines under certain conditions is further confirmed by the acceleration caused by $PbEt_4$; results with $CHMe:CH_2$ are even more striking. Other reactions unaffected by O_2 are association at the surface, gas-phase bimol. association, and gas-phase bimol. metathesis. Under analogous conditions $CHMe:CH_2$ yields mainly $CHMeCl:CH_2Cl$ and $CH_2:CH:CH_2Cl$. $CMe_2:CH_2$ at higher temp. reacts by addition and substitution. Below 240° , above which the reaction becomes violent, all activity is suppressed by 5% of O_2 , showing that both changes involve radical chain mechanism. Low $[O_2]$ strongly catalyses the substitution of Cl into olefines whereas larger concns. cause the expected inhibition. Experimental conditions, especially temp., are very important in defining the magnitude of the effect, which appears to be much more pronounced although more critically dependent on the catalyst concn. with C_2H_4 . $CHMe:CH_2$ and $(CHMe)_2$ are also subject to positive catalysis by O_2 but to a smaller extent. C_2H_6 is a powerful inhibitor of the O_2 -catalysed Cl-substitution into olefines. The rate of production of HCl by substitution seems to vary linearly with $[C_2H_4]^2$, $[Cl_2]$, and $[O_2]$ for very small concns. The mechanism is one of chain initiation by radicals produced by interaction of olefine and O_2 rather than reaction of an association complex itself with Cl. Olefines act as inhibitors of the high-temp. chlorination of paraffins; $CHMe:CH_2$ appears the most effective. H. W.

Mechanism of polymerisation. V. Dimerisation of unconjugated pentadiene. A. AHMAD and E. H. FARMER (J.C.S., 1940, 1176—1178).— Δ^8 -Pentadiene (I) with 15% BF_3 in AcOH (24 hr.) gives *isopentenyl acetate* (?), b.p. 138° , and $OAc[CH_2]_3CHMe:OAc$ (?). In light petroleum at -15° and 0° , BF_3 does not polymerise (I); with undiluted (I) it gives an undistillable polymeric oil. Below 225° , (I) alone does not polymerise. Under N_2 in an autoclave, (I) at 250° gives 15% polymerisation (7—8% of dimeride), and at 280 — 290° , 90% polymerisation (25% of di-, 10—15% of tri-, and 60—65% of higher poly-merides). Fractionation gives a dimeride (II), $C_{10}H_{16}$, b.p. 176° (mainly 1-methyl-2-allylcyclohexene), and a trimeride, b.p. 120 — $122^\circ/1$ mm. In $COMe_2$, (II) is oxidised by 4% aq. $KMnO_4$ to HCO_2H and an oily acid. Vapour of (II) with Pd-C at 178 — 181° gives an oil, b.p. 185° , of composition $\sim C_{10}H_{15}$ (C_6H_4MePr + methylpropylcyclohexane or dimethylidicyclooctane), oxidised to α - $C_6H_4(CO_2H)_2$. Possible mechanisms are discussed.

E. W. W.

Synthesis of polyenes. II. Reactions of β -methylallyl chloride with sodamide in liquid ammonia. M. S. KHARASCH, W. NUDENBERG, and E. STERNFELD (J. Amer. Chem. Soc., 1940, 62, 2034—2036; cf. A., 1939, II, 498).— $CH_2:CMe:CH_2Cl$ (I) (1.5) and $NaNH_2$ (1.7 mols.) in NH_3 give 27% of β -dimethyl-n-hexadiene (II), m.p. -9° , b.p. $90.2^\circ/200$ mm. (cf. Bourguet *et al.*, A., 1930, 574), hydrogenated to Bu^t_2 and adding $(:CH:CO)_2O$ (III) in C_6H_6 at 80°

to give 5-methyl-3-isopropenyl-1:2:3:6-tetrahydro-phthalic anhydride (IV), m.p. 115 — 116° . $NaNH_2$ (0.88) and (I) (1 mol.) give α -chloro- β -dimethyl-n-hexadiene, b.p. 33 — $34^\circ/5$ mm., $160^\circ/752$ mm. [with (III) gives (IV); with $NaNH_2$ gives (II)], and some (II). $CH_2:CH:CH_2Cl$ (1) and $NaNH_2$ (0.5 mol.) give a chlorohexadiene, b.p. 46 — $47.5^\circ/96$ mm., and 30% of chloromethylvinylcyclohexene. The ultra-violet and infra-red absorption of (II) are determined.

R. S. C.

Partial reduction of acetylenes to olefines by use of an iron catalyst. A. F. THOMPSON, jun., and S. B. WATT (J. Amer. Chem. Soc., 1940, 62, 2555—2556).—Fe catalyst prepared from Fe-Al alloy and NaOH in EtOH at $100^\circ/1000$ lb. is excellent for reduction of acetylenes to olefines. Examples are $(:C:CMe_2:OH)_2$ and $CH_3:C:CMe:CH_2$ (gives $CH_2:CH:CMe:CH_2$), but C_2Ph_2 gives $(CH_2Ph)_2$.

R. S. C.

Fluorinated derivatives of ethane and ethylene. VI. Corrective data. A. L. HENNE and E. G. WIEST (J. Amer. Chem. Soc., 1940, 62, 2051—2052; cf. A., 1934, 1689).—The following data are recorded and shown to accord with expectation. $CCl_2:CF_2$, b.p. 18.9 — 19.0° (corr.). $CCl_3:CClF_2$, m.p. 40.6° , b.p. 91.5° . $CCl_2Br:CBrF_2$, f.p. 45.5° , b.p. 138.8 — 139.0° (corr.). $(CClBrF)_2$, f.p. 32.9 — 32.6° , b.p. 139.8 — 140.0° (corr.). $CCl_3:CF_3$, f.p. 14.2° , b.p. 45.9° (corr.).

R. S. C.

Peroxide effect in addition of reagents to unsaturated compounds. XXV. Effect of metals on the addition of hydrogen bromide to allyl bromide. M. S. KHARASCH, W. R. HAEFELE, and F. R. MAYO (J. Amer. Chem. Soc., 1940, 62, 2047—2051; cf. A., 1940, II, 61).—Promotion of abnormal additions by metals depends on ready reaction of the metal with HBr, and inability of the halide to promote the normal reaction or hinder the abnormal one. This is demonstrated for Fe, HBr, and $CH_2:CH:CH_2Br$, and by the varying results with other metals. Fe induces also abnormal addition of HBr to $CH_2:CH:CH_2Cl$. The reaction mechanism (discussed) is that for reaction without Fe. The mechanism proposed by Urushibara *et al.* (A., 1938, I, 628) for the normal addition is refuted.

R. S. C.

Melibiotol and maltitol. M. L. WOLFROM and T. S. GARDNER (J. Amer. Chem. Soc., 1940, 62, 2553—2555).—Melibiose and H_2 -Ni-kieselguhr in H_2O at $150^\circ/190$ atm. give melibiotol, m.p. 173° (lit., a syrup), $[\alpha]^{24} +116^\circ$ in H_2O (nonabenzoate, m.p. 157° , $[\alpha]^{25} +123^\circ$ in $CHCl_3$), hydrolysed to *d*-galactose and sorbitol. Maltitol nona-acetate is obtained cryst., having m.p. 86 — 87° , $[\alpha]^{20} +84^\circ$ in $CHCl_3$ (cf. Karrer *et al.*, A., 1937, II, 83). Most of the $[\alpha]$ of these and similar α -glucosides is due to the lactol C.

R. S. C.

Synthesis of esters of phosphoric acid related to phosphatides. H. N. CHRISTENSEN (J. Biol. Chem., 1940, 135, 399—401).— H_3PO_4 and $(CH_2)_2NH$ at 105° yield aminoethyl H_2 phosphate, m.p. 240° (decomp.). Cetyl alcohol in boiling CCl_4 yields, with $POCl_3$, cetyl, and with $Cl[CH_2]_2POCl_2$, β -chloroethyl cetyl *H* phosphate, m.p. 54.5° , converted by EtOH- NH_3 in a sealed tube at 110° into β -aminoethyl cetyl *H*

phosphate, m.p. 226° (decomp.) (corr.). All these acids are purified through the Ba salts. A. LI.

Factors influencing polysulphone formation. M. S. KHARASCH and E. STERNFELD (J. Amer. Chem. Soc., 1940, **62**, 2559—2560).—Ascaridole + aq. or alcoholic mineral acid catalyses formation of *poly-sulphones*, decomp. 210—235°, m.p. 125—160° (decomp.), and decomp. 245—265°, from $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$, $\text{CMe}_2\cdot\text{CHMe}$, or $\text{CH}_2\cdot\text{CHCl}$, respectively. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and, more so, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ are inhibitors for this reaction. C_2HCl_3 and $\text{CMe}_2\cdot\text{CHBu}^v$ do not form polysulphones, but are not inhibitors. Other chain-breakers do not act as inhibitors. R. S. C.

Structure of compounds containing S-O and S-Cl bonds.—See A., 1940, I, 434.

Preparation of trioctoin. J. L. HARTWELL (Amer. J. Path., 1940, **16**, 313—316).—The prep. of pure $n\text{-C}_7\text{H}_{15}\cdot\text{COCl}$ and its condensation with glycerol in the presence of $\text{C}_5\text{H}_5\text{N}$ to yield trioctoin are described. C. J. C. B.

Direct esterification of higher fatty acids with glycerol. III. **Formation of mono- and di-stearin.** S. KAWAI and H. NOBORI (J. Soc. Chem. Ind. Japan, 1940, **43**, 170B; cf. A., 1940, II, 336).—Stearic acid with 1.2 or 1.4 mols. of glycerol at 180° for several hr., then at 240—245° for 0.5—1 hr., yields mono- (20%) and di-stearin (up to 70%). A part of the product from commercial stearin sol. in 85% EtOH at 60° has emulsifying properties. A. LI.

Condensations. XIII. **Alkylation of ethyl isobutyrate and other esters by means of sodium triphenylmethyl and alkyl halides.** B. E. HUDSON, jun., and C. R. HAUSER (J. Amer. Chem. Soc., 1940, **62**, 2457—2459).— $\text{CHR}_2\cdot\text{CO}_2\text{Et}$, CPh_3Na , and R'I give good yields of $\text{CR}_2\text{R'}\cdot\text{CO}_2\text{Et}$. $\text{Pr}^i\text{CO}_2\text{Et}$ thus gives 58% of $\text{CMe}_2\text{Et}\cdot\text{CO}_2\text{Et}$, 42% of $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$, and 55% of $\text{Bu}^i\text{CO}_2\text{Et}$. $\text{CHMeEt}\cdot\text{CO}_2\text{Et}$, b.p. 132° (corr.) (lit., 133.5°), gives 61% of *Et* α -methyl- α -ethyl-*n*-valerate, b.p. 81° (corr.)/20 mm. $\text{Bu}^i\text{CO}_2\text{Et}$ gives 22% of $\text{CHEtPr}^i\cdot\text{CO}_2\text{Et}$. EtOAc , CH_2PhCl , and CPh_3Na do not react. R. S. C.

Compounds of lead halides with organic salts.—See A., 1940, I, 444.

Oxidation of [long-chain] unsaturated fatty acids.—See B., 1940, 725.

Linolenic acid and its isomerides. J. W. McCUTCHEON (Canad. J. Res., 1940, **18**, B, 231—239; cf. A., 1938, II, 347).—Linolenic acid (prepared by a modification of Rollet's method, using Et_2O instead of AcOH), m.p. -16.25° to -17°, with Br in Et_2O yields the cryst. hexabromide (I), m.p. 181.9° (corr.), and two isomerides (sol. in Et_2O , separated by *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$), one gummy, m.p. 145—150°, and the other liquid, both debrominated to an acid identical with that obtained from (I), and (?) with the natural acid. B.p. 2.5—6.5 mm., *d*, *n*, and I val. of the Et ester are recorded. A. LI.

Action of lead tetra-acetate on hydroxylated fatty acids and related compounds. I. **Hydroxylated oleic acid, ethyl oleate, and oleyl**

alcohol. II. **Hydroxylated ricinoleic acid and castor oil.** J. T. SCANLAN and D. SWERN (J. Amer. Chem. Soc., 1940, **62**, 2305—2309, 2309—2311).—I. Hydroxylation of Et oleate, oleic acid, and oleyl alcohol is improved and the products are converted in AcOH by Pb_3O_4 into $\text{C}_8\text{H}_{17}\cdot\text{CHO}$ and $\text{CHO}\cdot[\text{CH}_2]_7\cdot\text{R}$ ($\text{R} = \text{CO}_2\text{Et}$, CO_2H , or $\text{CH}_2\cdot\text{OH}$). The effect of impurities on yields is described. Yields are poor with olive, peanut, and lard oils.

II. Hydroxylation and Pb_3O_4 -AcOH oxidation of castor oil (not ricinoleic acid) gives $\text{CHO}\cdot[\text{CH}_2]_7\cdot\text{CHO}$, glycerol, and $\text{C}_6\text{H}_{13}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, b.p. 56—58°/0.1 mm. [semicarbazone, new m.p. 165—165.5°; 2:4-dinitrophenylhydrazone, m.p. 126°, previously reported (m.p. 124°) as derived from $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$; oxidised by air to the acid, m.p. 0—1°, b.p. 135—138°/5 mm. (*p*-phenylphenacyl ester, m.p. 77.5—78°; amide, new m.p. 130—130.5°)]. R. S. C.

Action of hydrogen bromide and oxygen on various ethenoid compounds and the influence of pyrocatechol. O. SIMAMURA (Bull. Chem. Soc. Japan, 1940, **15**, 292—297).—A mixture of HBr and O_2 in the dark has no effect on solutions of C_2Ph_4 , dimethylmaleic anhydride, or phenanthrene in C_6H_6 . With Et α -dicarbethoxy- α -bromoglutaconate (I) in CCl_4 , Br is liberated. With Et_2 α -dicarbethoxy- α -methylglutaconate in CCl_4 little Br is liberated and the product contains Br corresponding with the addition of a mol. of HBr. With $\text{CH}_2\cdot\text{CPh}_2$ Br is liberated. Me_2 dimethylmaleate and Me_2 dimethylfumarate (II) behave as does (I). With the compound $\text{C}_{30}\text{H}_{42}\text{O}_{16}$, m.p. 86° (Guthzeit and Hartmann, A., 1910, i, 386), in CCl_4 , Br is liberated. These reactions accord with the mechanism suggested by Urushibara *et al.* (A., 1938, II, 401). *o*- $\text{C}_6\text{H}_4(\text{OH})_2$ markedly inhibits the reaction with (II) and with allyl bromide, presumably by suppressing the initial reaction of the chain. F. J. G.

Sulphonation reactions with sulphuryl chloride. II. **Photochemical sulphonation of aliphatic acids with sulphuryl chloride.** M. S. KHARASCH, T. H. CHAO, and H. C. BROWN (J. Amer. Chem. Soc., 1940, **62**, 2393—2397; cf. A., 1940, II, 3).— SO_2Cl_2 with lower aliphatic acids (except AcOH) in light gives β - or γ -sulphocarboxylic anhydrides and with higher acids gives sulphonyl chlorides by substitution in other positions. Varying amounts of Cl-acids are also obtained. A reaction mechanism is postulated involving Cl atoms and org. radicals. Properties of the anhydrides are reported. β -Sulphopropionic (I), m.p. 76—77°, and isobutyric anhydride, b.p. 135—145° (decomp.)/3—5 mm., and (? β - or γ -) sulpho-*n*-butyric anhydride, an oil, are thus obtained. $\text{Bu}^i\text{CO}_2\text{H}$, cyclohexanecarboxylic, and lauric acids give 25—60% of RSO_2Cl . NH_2Ph sulphonanilido-cyclohexanecarboxylate is described. With H_2O the anhydrides give sulphocarboxylic acids, with NH_2Ph in C_6H_6 they give NH_2Ph propion-, m.p. 216°, and isobutyranilide- β -sulphonate, decomp. 238°, and *n*-butyranilide- β - + γ -sulphonates; with liquid NH_3 , (I) gives NH_4 propionamide- β -sulphonate, m.p. 179°. R. S. C.

Derivatives of methylacetaldehyde. R. L. SHRINER and A. G. SHARP (J. Amer. Chem. Soc.,

1940, 62, 2245).— $\text{CH}_2\text{:CMe}\cdot\text{CHO}$ gives a *semicarbazone*, m.p. 197.5—198°, *p-nitro-*, m.p. 161—163°, and 2:4-dinitro-phenylhydrazones, m.p. 206—206.5°, and 1-phenyl-4-methyl- Δ^2 -pyrazoline, m.p. 73—74°.

R. S. C.

β -Diketones. Synthesis, structure, and bactericidal properties. C. D. HURD and C. D. KELSO (J. Amer. Chem. Soc., 1940, 62, 2184—2187).—Claisen condensation of COMeBu^a or $\text{COMe}\cdot\text{C}_6\text{H}_{13}$ with EtOAc gives $\text{COMe}\cdot\text{CH}_2\cdot\text{COBu}^a$ (II), b.p. 83—85°/21 mm., and $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_{13}\cdot n$, b.p. 129—131°/33 mm., respectively. (II) is obtained (10%) also from $\text{CH}_2\text{Ac}\cdot\text{COCl}$ (III) and MgBu^aBr in $\text{Et}_2\text{O}\cdot\text{N}_2$ at -25° and its structure is confirmed by condensation with N_2H_4 and oxidation of the product by KMnO_4 to pyrazole-3:5-dicarboxylic acid; with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ it gives 3-methyl-5-n-butylpyrazole-1-carboxylamide, m.p. 89—90°. $n\text{-C}_7\text{H}_{15}\cdot\text{MgBr}$ or $n\text{-C}_8\text{H}_{17}\cdot\text{MgBr}$ with (III) gives hendecane-, b.p. 93—95°/2—3 mm. (lit., 118°/5 mm.), and dodecane- $\beta\delta$ -dione, b.p. 104—105°/2—3 mm. (lit., 150°/15 mm.), respectively. $n\text{-C}_6\text{H}_{13}\cdot\text{CHMe}\cdot\text{MgBr}$ and (III) give ϵ -methylhendecane- $\beta\delta$ -dione, b.p. 101—102°/2 mm. MgBu^aBr with (III) in Et_2O -air at -50° gives $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Bu}^a$, b.p. 95°/15 mm. (*semicarbazone*, m.p. 102°), also obtained from $\text{CHAc}\cdot\text{CO}$ and Bu^aOH . $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, (I), and NaOEt in xylene give 53% of Δ^2 -dodecene- $\delta\zeta$ -dione, m.p. 98—99°, with some $\text{CHMe}[\text{C}(\text{CHMe})\cdot\text{CO}_2\text{Et}]_2$, b.p. 110—114°/5 mm. $\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, (I), and $\text{NaOEt}\cdot\text{EtOH}$ give 54% of Δ^a -hendecene- $\gamma\epsilon$ -dione, m.p. 69—70°. In spite of formal resemblance of the dienolic forms of the diketones to alkylresorcinols, the saturated ketones are only weak bactericides against *B. typhosus* and ineffective against *S. aureus*. The unsaturated ketones are mildly effective against both organisms.

R. S. C.

Reduction of aldoses at the dropping mercury cathode. Determination of the aldehydo-form in aqueous solutions. S. M. CANTOR and Q. P. PENISTON (J. Amer. Chem. Soc., 1940, 62, 2113—2121).—Aldoses are reduced at the dropping Hg cathode, owing to presence of the aldehydo-form in highly mobile equilibrium with the cyclic forms. The amounts thus determined for four hexoses and four pentoses are correlated with rates of mutarotation. The amounts are very small except for allose and ribose. They are greater for pentoses than for hexoses, but in both cases are greatly influenced by configuration.

R. S. C.

Mutarotation of *d*-glucose in absolute methanol and in ethanol-water mixtures.—See A., 1940, I, 442, 443.

Derivatives of the aldehydrol form of sugars.

III. Carbon one asymmetry. M. L. WOLFROM, M. KONTSGBERG, and F. B. MOODY (J. Amer. Chem. Soc., 1940, 62, 2343—2349; cf. A., 1938, II, 126).—Demercaptalation (method: A., 1939, II, 202) of *d*-mannose Et_2 mercaptal penta-acetate (I) gives aldehydo-*d*-mannose penta-acetate aldehydrol (II), $+\text{COMe}_2$, m.p. 68—70°, $[\alpha]_D^{25} + 24^\circ \rightarrow +9^\circ$ in CHCl_3 , $[\alpha]_D^{25} + 26^\circ$ (stable) in H_2O , which in air at \leq room temp. loses COMe_2 and gives a syrup (III). In MeOH , (III) gives aldehydo-*d*-mannose penta-acetate

Me semiacetal, m.p. 102—104°, $[\alpha]_D^{25} + 27.5^\circ \rightarrow +17^\circ$ in CHCl_3 , also obtained from (I) and converted by $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ into aldehydo-*d*-mannose hepta-acetate. aldehydo-*d*-Galactose penta-acetate aldehydrol has $[\alpha]_D^{25} + 4^\circ$ (stable) in H_2O . AcBr and (III) at room temp. give 1-bromo-aldehydo-*d*-mannose hexa-acetate, m.p. 115—116°, $[\alpha]_D^{25} + 92^\circ$ in CHCl_3 . 1-Bromo-aldehydo-*l*-rhamnose penta-acetate, m.p. 112—113°, $[\alpha]_D^{25} - 103^\circ$ in CHCl_3 , is similarly prepared. aldehydo-*d*-Mannose penta-acetate with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 0° , followed by 50% MeOH , gives α -1-methoxy-aldehydo-*d*-mannose hexa-acetate, m.p. 84—85°, $[\alpha]_D^{25} + 23^\circ$ in CHCl_3 , and thence $(\text{Ac}_2\text{O}\cdot\text{AcOH})\cdot\text{ZnCl}_2$, followed by 50% MeOH the β -isomeride, m.p. 95.5—96°, $[\alpha]_D^{25} + 11^\circ$ in CHCl_3 , and $(\text{AlCl}_3\cdot\text{CHCl}_3)$ 1-chloro-1-methoxy-aldehydo-*d*-mannose penta-acetate, m.p. 116—118°, $[\alpha]_D^{25} + 71^\circ \rightarrow +25^\circ$ in 24 hr. in CHCl_3 . α -, m.p. 103—104°, $[\alpha]_D^{25} + 3.8^\circ$, and β -1-Methoxy-aldehydo-*d*-glucose hexa-acetate, m.p. 61—62°, $[\alpha]_D^{25} - 3^\circ$ in CHCl_3 , α - (IV), m.p. 101°, $[\alpha]_D^{25} + 3.5^\circ$ in CHCl_3 , and β -1-methoxy-aldehydo-*d*-galactose hexa-acetate (V), m.p. 123—124°, $[\alpha]_D^{25} + 2.1^\circ$ in CHCl_3 , α -, m.p. 67—68°, $[\alpha]_D^{25} - 34^\circ$ in CHCl_3 , and β -1-methoxy-aldehydo-*l*-arabinose penta-acetate, m.p. 76—77°, $[\alpha]_D^{25} - 27^\circ$ in CHCl_3 , are prepared with the fully acetylated aldehydo-forms from the appropriate semiacetal. $\text{HCl}\cdot\text{Et}_2\text{O}$ at 0° converts (IV) or (V) into 1-chloro-1-methoxy-aldehydo-*d*-galactose penta-acetate, m.p. 155—156°, $[\alpha]_D^{25} - 38^\circ \rightarrow +15^\circ$ in 24 hr. in CHCl_3 , $[\alpha]_D^{25} - 53^\circ \rightarrow -42.5^\circ$ in 10 hr. in C_6H_6 ; the corresponding OEt -compound suffers replacement of Cl by OH during all reactions in "anhyd." solvents. *l*-Arabinose Me_2 mercaptal tetra-acetate, CdCO_3 , and HgCl_2 in boiling, abs. MeOH give the Me_2 acetal tetra-acetate, m.p. 81°, $[\alpha]_D^{25} - 22^\circ$ in CHCl_3 , converted by 0.1N- NaOMe into *l*-arabinose Me_2 acetal, m.p. 121—122°, $[\alpha]_D^{25} + 20^\circ$ in H_2O ; the Et_2 acetal, m.p. 109°, $[\alpha]_D^{25} + 16^\circ$ in H_2O , and its acetate, m.p. 59°, $[\alpha]_D^{25} - 17.5^\circ$ in CHCl_3 , are similarly prepared. 1-Bromo-aldehydo-*d*-galactose hexa-acetate and Ag_2CO_3 in boiling abs. EtOH give aldehydo-*d*-galactose Et semiacetal. *d*-Gluco-*d*-guloheptose Et_2 mercaptal hepta-acetate, m.p. 99—100°, $[\alpha]_D^{25} - 12^\circ$ in CHCl_3 , is obtained from the mercaptal by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$.

R. S. C.

Use of the benzyl radical in synthesis of methylated sugars. II. 4:6-Dimethylgalactose. J. S. D. BACON, D. J. BELL, and J. LORBER (J.C.S., 1940, 1147—1150).—That the dimethylgalactose obtained by Hirst *et al.* (cf. A., 1939, II, 495) from damson gum is not 4:6-dimethyl- α -galactose (I), m.p. 131—133°, $[\alpha]_D^{25} + 133^\circ \rightarrow 76.9^\circ$ in H_2O , is proved by synthesis of (I). 4:6-Benzylidene- β -methylgalactoside 2:3-diacetate gives (cf. Bell *et al.*, A., 1940, II, 205) the 4:6- CH_2Ph derivative, m.p. 132.5—133.5°, $[\alpha]_D^{25} + 50.2^\circ$ (this and subsequent rotations in CHCl_3), of 2:3-dibenzyl- β -methylgalactoside, m.p. 70—71°, $[\alpha]_D^{18} + 10.6^\circ$, which yields (Purdie) a 4:6- Me_2 derivative, m.p. 68—69°, $[\alpha]_D^{25} + 3.05^\circ$. This with Na in EtOH yields 4:6-dimethyl- β -methylgalactoside (II), m.p. 140°, $[\alpha]_D^{25} - 41.5^\circ$, hydrolysed (N-HCl) to (I). 4:6-Benzylidene- β -methylgalactoside gives a 2:3-di-*p*-toluenesulphonate, m.p. 168—170°, $[\alpha]_D^{25} + 29.5^\circ$, hydrolysed to β -methylgalactoside 2:3-di-*p*-toluenesulphonate, m.p. 149—150°, $[\alpha]_D^{19} + 18.4^\circ$. Purdie methylation of this gives the 2:3-di-*p*-toluenesulphonate,

a syrup, $[\alpha] +5-6^\circ$, of (II), from which it is also obtained. In cold MeOH-HCl (I) shows increasing $[\alpha]$, indicating that furanoside is not formed, and that there is Me at C₄; further (Purdie) methylation, hydrolysis, and treatment with EtOH-NH₂Ph gives 2:3:4:6-tetramethylgalactose anilide, m.p. 196—197°. With NPh-NH₂, (I) gives its osazone, identical with that prepared from 2:4:6-trimethylgalactose. E. W. W.

isoPropylidene derivatives of the mercaptals of monosaccharides. V. 5:6-isoPropylidene derivative of *d*-galactose dibenzyl mercaptal and the 6-methyl derivative of *d*-galactose. E. PACSU and S. M. TRISTER (J. Amer. Chem. Soc., 1940, 62, 2301—2304).—The mercaptal, m.p. 112.5°, $[\alpha]_D^{20} +17.4^\circ$ in CHCl₃ (A., 1939, II, 494), is proved to be 5:6-isopropylidenegalactose (CH₂Ph)₂ mercaptal and the structure of 6-methylgalactose (II) (Munro *et al.*, A., 1936, 826) is confirmed. HgO-HgCl₂-EtOH etc. converts (I) into 5:6-isopropylidene- β -ethylgalactofuranoside, a syrup, $[\alpha]_D^{25} -70.0^\circ$ in H₂O, which consumes 1 HIO₄ (giving no CH₂O) and with MeI-Ag₂O gives 2:3-dimethyl-5:6-isopropylidene- β -ethylgalactofuranoside, a liquid, stable to HIO₄ and converted by 0.05N-HCl at 90° into 2:3-dimethylgalactose (III), $[\alpha]_D^{25} +64.7^\circ \rightarrow +80.9^\circ$ in 90 min. in H₂O, $[\alpha]_D^{25} +17.2^\circ$ in CHCl₃ [anilide, m.p. 128—129° (lit. 130—131°)]. The structure of (III) is confirmed by consumption of 2 HIO₄ and conversion by NPh-NH₂-AcOH into 3-methylgalactosazone, m.p. 176—179°, $[\alpha]_D^{25} +63.5^\circ$ in C₅H₅N. Galactose (CH₂Ph)₂ mercaptal and H₂SO₄-COMe₂ at 0° give the CMe₂ derivative, methylated as Na salt by MeI (twice) to the ether, which with boiling HCl-EtOH-H₂O gives 6-methylgalactose (CH₂Ph)₂ mercaptal, m.p. 130°, $[\alpha]_D^{25} -27.1^\circ$ in C₅H₅N. With HgO-HgCl₂ etc. this gives 6-methyl- β -methylgalactofuranoside, a syrup, $[\alpha]_D^{20} -78.7^\circ$ in H₂O, hydrolysed by boiling 0.05N-HCl to (II), m.p. 113—114°, $[\alpha]_D^{25} +137.2^\circ \rightarrow +77.0^\circ$ in 6 hr. in H₂O [consumes 4 HIO₄; phenylhydrazine, m.p. 117.5° (lit., 182—183°, 179°), $[\alpha]_D^{25} +22.4^\circ \rightarrow +13.6^\circ$ in 24 hr. in C₅H₅N; osazone, m.p. 200°, $[\alpha]_D^{25} +141.0^\circ \rightarrow +91.8^\circ$ in 24 hr. in C₅H₅N]. R. S. C.

Synthesis of 1- β -glucosidofructose. E. PACSU (J. Amer. Chem. Soc., 1940, 62, 2568).—A question of priority. R. S. C.

Sterol glucosides from expressed soya-bean oil. M. H. THORNTON, H. R. KRAYBILL, and J. H. MITCHELL, jun. (J. Amer. Chem. Soc., 1940, 62, 2006—2008).—Treatment of crude expeller soya-bean oil with Al silicate and elution of the latter with COMe₂ gives sterol glucosides, darken at 250—255°, m.p. 267—270° (decomp.) (tetra-acetate, m.p. 165—166°, $[\alpha]_D^{20} -24.5^\circ$ in CHCl₃), which with H₂SO₄-EtOH give Et glucoside (identified by conversion into *d*-glucobenzimidazole) and sterols resembling those of the oil and containing ~24% of stigmasterol. R. S. C.

Composition of hemicellulose isolated from maple wood. R. L. MITCHELL and G. J. RITTER (J. Amer. Chem. Soc., 1940, 62, 1958—1959).—Hemicellulose fractions are prepared from maple hemicellulose by boiling H₂O, cold 2% Na₂CO₃, cold 4% NaOH, and boiling 10% NaOH, successively. The

products are isolated by pptn. by EtOH (from the aq. extract also by COMe₂). Uronic anhydride, xylan, OMe, Ac, and $[\alpha]_D$ are recorded for each fraction. Approx. min. mol. wts. (from I val.) increase from 1070 to 10,500. R. S. C.

Chemistry of wood. VII. Esters and ethers of the water-soluble polysaccharides of larch wood. F. C. PETERSON, A. J. BARRY, H. UNKAUF, and L. E. WISE (J. Amer. Chem. Soc., 1940, 62, 2361—2365; cf. A., 1935, 478).—Arabogalactans (I) from Eastern, Western, and European larch wood are similar. Fractional pptn. of the undegraded acetate, propionate, and benzoate gives fractions of similar acyl content but differing $[\alpha]$, reducing val., η , and araban content. (I) is thus not homogeneous. A fully methylated product (44.1% OMe) is prepared by Me₂SO₄-COMe₂-aq. NaOH. R. S. C.

Isolation of glucosamine and chondrosamine. Z. E. JOLLES and W. T. J. MORGAN (Biochem. J., 1940, 34, 1183—1190).—The method for the isolation of 10—30 mg. of glucosamine (I) and chondrosamine takes advantage of the low solubility in H₂O of 2-hydroxynaphthylidene-glucosamine, m.p. 202—203°, $[\alpha]_{5461} +274^\circ$ in MeOH (217° after 18 hr.) (hydrochloride sinters at 200°), and -chondrosamine, m.p. 175—178° (decomp.), $[\alpha]_{5461} +287^\circ$ in MeOH (+258° after 18 hr.). Sugars and NH₂-acids do not interfere. The corresponding *p*-nitrobenzylidene compounds, decomp. 182—184° and 175—176°, the 4-hydroxy-3-methoxybenzylidene compounds, m.p. 184° (decomp.) and 153—155° (glucosamine compound, $[\alpha]_{5461} +64^\circ$ in C₅H₅N), and the corresponding *p*-nitrocinnamylidene compounds, m.p. 187° (decomp.) and 172—173° respectively (glucosamine compound, $[\alpha]_{5461} +57.6^\circ$ in C₅H₅N changing to +41.5° overnight), are described. Part of the NH₂-sugar of the sp. polysaccharide of *B. dysenteriae* (Shiga) is (I). W. McC.

Aromatic sulphonic acids as reagents for amino-acids. D. G. DOHERTY, W. H. STEIN, and M. BERGMANN (J. Biol. Chem., 1940, 135, 487—496).—The solubility in N-HCl at 0° of the salts of 26 aromatic sulphonic acids with 18 NH₂-acids has been investigated. The solubility products of the less sol. salts are recorded. Analyses of the following *sulphonates*, likely to be of use in the isolation or determination of NH₂-acids, are given: 1-leucine (+H₂O), dl-phenylalanine, and 1-histidine 2-bromotoluene-5-; 1-histidine and 1-arginine 3:4-dichlorobenzene-; dl-phenylalanine 2:5-dibromo- and 2:4:5-trichlorobenzene-; glycine, dl-alanine, 1-leucine, dl-phenylalanine (+H₂O), 1-arginine, and 1-histidine O-benzyl-p-phenol- (+0.75H₂O); 1-leucine (+H₂O), dl-phenylalanine (+H₂O), 1-tyrosine (+H₂O), 1-arginine (+0.5H₂O), and 1-lysine O-(2:4-dinitrophenyl)-p-phenol- (+2H₂O); 1-leucine and dl-phenylalanine O-p-toluenesulphonyl-p-phenol- (+H₂O); dl-phenylalanine (+2H₂O), 1-tyrosine, and 1-arginine 2:6-diiodophenol-4- (+2H₂O); glycine, 1-leucine, 1-hydroxyproline, dl-phenylalanine, 1-arginine (+2H₂O), 1-histidine (+H₂O), and 1-lysine 5-nitronaphthalene-1- (+3H₂O); 1-leucine (+2H₂O), 1-phenylalanine, and 1-tyrosine 2:4-dinitro-1-naphthol-7- (+H₂O); and 1-leucine 2-naphthol-7-. Salts of arginine, histidine, and lysine contain 2 mols. of sulphonic to 1 of NH₂-acid.

The prep. of NH_4 O-(2 : 4-dinitrophenyl)- (+H₂O) and Na O-*p*-toluenesulphonyl-*p*-phenolsulphonic acid (+2H₂O), starting with *p*-OH·C₆H₄·SO₃Na, NaOH, and 1 : 2 : 4-C₆H₃Cl(NO₂)₂ and *p*-C₆H₄Me·SO₂Cl respectively, is described. 1-C₁₀H₇NO₂ with conc. H₂SO₄ yields 5-nitronaphthalene-1-sulphonic acid (+2H₂O) (purified by the glycine salt), converted via the Na salt and acid chloride into the amide.

A. LI.

Preparation of alkylamino-acids and their electrometric titration. W. COCKER and J. O. HARRIS (J.C.S., 1940, 1290—1294; cf. A., 1937, II, 488).—SO₂Ph·NH·CH₂·CO₂H (I) and SO₂Ph·NH·CHMe·CO₂H (II) with RI at 100° yield *N*-benzenesulphonyl-*N*-*n*-butyl-, m.p. 101—102°, -*n*-amyl-, m.p. 84°, and -isobutyl-glycine, m.p. 90—91°, and -ethyl-, m.p. 145°, and -*n*-propyl- α -alanine, m.p. 117°, hydrolysed (60% H₂SO₄) to *N*-*n*-butyl-, m.p. 192° (inst.) (phenylcarbamido-compound, m.p. 127—128°), -*n*-amyl- (III), m.p. 201° (inst.) (phenylhydantoin, m.p. 111°), and -isobutyl-glycine, m.p. 188° (phenylcarbamido-compound, m.p. 86—87°), and -*n*-ethyl-, m.p. 302—303° (inst.), and -*n*-propyl- α -alanine, m.p. 302—303°. The acid and basic dissociation consts. (K_A and K_B) of these acids, except (III), and those of glycine, NHMe·CH₂·CO₂H, NH₂·CH₂·CO₂H, NH₂·CHMe·CO₂H, and NHMe·CHMe·CO₂H, have been determined by electrometric titration (H₂ electrode). Substitution of NH₂ by alkyl slightly decreases K_A (K_A being const. for different alkyl groups), and considerably decreases K_B , in accordance with the "zwitterion" theory. (I) and (II) do not react with higher alkyl halides; the Et esters of (I) and (II) gave better alkylation, the nitriles better still. By hydrolysis (conc. HCl) of the alkylated nitrile, *N*-benzenesulphonyl-*N*-*n*-hexylglycine, m.p. 85—86°, is obtained. Partial hydrolysis (conc. H₂SO₄) of benzenesulphonyl-*n*-amylaminoacetonitrile yields the amide, m.p. 94°, hydrolysed (NaOH) in small yield to the acid.

A. LI.

Synthesis of pantothenic acid. D. W. WOOLLEY (J. Amer. Chem. Soc., 1940, 62, 2251—2252).—Synthesis of Na pantothenate from OH·CH₂·CMe₂·CH(OH)·CO₂H and β -alanine is outlined.

R. S. C.

Reactions of nitriles and related compounds with sulphur in presence of amines. Synthesis of quaternary ammonium thiocyanates. C. R. McCROSKEY, F. W. BERGSTROM, and G. WAITKINS (J. Amer. Chem. Soc., 1940, 62, 2031—2034).—At 200—210° NMe₄CN gives NMe₃ and MeCN. NMe₃ does not recombine with MeCN or PhCN. MeCN, NMe₃, and S in MeOH at 200—210° give 25% of H₂O-sol. thiocyanates, including NMe₄ thiocyanate (I), m.p. 296—297°, and 10—25% of H₂O-sol. thiocyanates are formed by use of other nitriles, NH₂Ac, NH₄OBz, NH₂Bz, or NH₄OAc. (II) or (III) (below) dissociates at 200—210° to give by recombination mixed quaternary thiocyanates including (I). NH₃ also gives thiocyanates. MeSH, Me₂S, and probably other products are also formed in the above reactions. NMe₃ and EtSCN at 100—110° give NMe₃Et thiocyanate (II), m.p. 131—132°. CH₂Ph·NMe₃ thiocyanate (III), m.p. 117—118°, is obtained from CH₂Ph·SCN and

NMe₃ in MeOH at room temp. (3 days). PhSCN and NMe₃ (excess) at 100—110° give a mixture; in MeOH at 200—210° they give (I). MeSeCN and NMe₃ at room temp. give NMe₄ selenocyanate, m.p. 267—268° (decomp.).

R. S. C.

Hydrogen cyanide. XII. Asymmetry of the tetrapolymeride of hydrogen cyanide. L. E. HINKEL and T. I. WATKINS (J.C.S., 1940, 1206—1208).—The aminoiminosuccinonitrile (I) structure proposed (cf. Hinkel *et al.*, A., 1937, II, 433) for (HCN)₄ (II) is confirmed. In EtOAc, (II) gives the dl-8-camphorsulphonate, m.p. 176—182° (variable) (decomp.), of (I), which in boiling EtOAc gives the l-diastereoisomeride, m.p. 237° (decomp.), strongly laevorotatory in C₅H₅N, which is hydrolysed in H₂O to an optically inactive base.

E. W. W.

Manufacture of trichloroacetonitrile.—See B., 1940, 726.

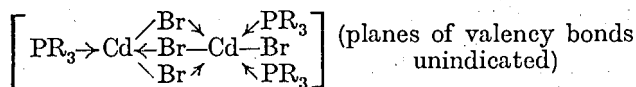
Constitution of complex metallic salts. XI. Structure of the tertiary phosphine and arsine derivatives of cadmium and mercuric halides. R. C. EVANS, F. G. MANN, H. S. PEISER, and D. PURDIE. XII. Bridged compounds containing two different metallic atoms. XIII. Stability of the 4-covalent auric complex. F. G. MANN and D. PURDIE (J.C.S., 1940, 1209—1230, 1230—1235, 1235—1239; cf. A., 1939, I, 61; II, 536).—XI. *tert*. Phosphines and arsines yield three types of compounds with Cd halides: class 1, [(R₃P(As))₂CdX₂]; class 2, [(R₃P(As))₂(CdX₂)₂]; class 3, [(R₃P(As))₃(CdX₂)₂], whilst five types are obtained with Hg^{II} halides: class A, [(R₃P(As))₃HgX₂]; class B, [(R₃P(As))₂(HgX₂)₂]; class C, [(R₃P(As))₂(HgX₂)₃]; class D, [(R₃P(As))₂(HgX₂)₄]; class E, [(R₃P(As))₃(HgX₂)₂]. Members of class 1 are prepared by shaking aq. CdX₂ or CdX₂ in EtOH with the theoretical amount of PR₃ or AsR₃; they vary in stability, some discarding half their PR₃ or AsR₃ and changing to the corresponding compound of class 2.

The structure is probably $\left[\begin{array}{c} R_3P \searrow \\ \quad \quad \quad \nearrow R_3P \\ R_3P \nearrow \end{array} \begin{array}{c} X \\ \quad \quad \quad X \\ \quad \quad \quad X \end{array} \right]$ (valency

bonds in normal type lie in the plane of the paper, those in heavy type project tetrahedrally above, those in dotted type tetrahedrally below, this plane). Preps. of the following members of this class (*dihalo-genobis-phosphine-* or *-arsine-cadmium*) are given: [(PEt₃)₂CdI₂], m.p. 132—134°; [(PEt₃)₂CdBr₂], m.p. 103—104°; [(PPr^{*i*})₂CdCl₂], an unstable oil; [(PPr^{*i*})₂CdBr₂], m.p. 75—77°; [(PPr^{*i*})₃CdI₂], m.p. 72—73°; [(PBu^{*i*})₃CdBr₂] and [(PBu^{*i*})₃CdI₂], oils; [(PPh₃)₂CdBr₂], m.p. 225—226°; [(PPh₃)₂CdI₂], m.p. 243°; [(AsEt₃)₂CdI₂], m.p. 79—81°; [(AsPr^{*i*})₃CdI₂], m.p. 27—29°. Class 2 compounds are formed by interaction of class 1 compounds with 1 mol. of CdX₂ in hot EtOH; they are usually more stable than those of class 1. The most likely structure is the tetrahedral *trans*-symmetric structure,

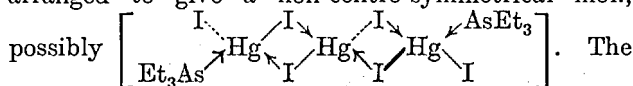
$\left[\begin{array}{c} Br \quad \quad Br \\ \quad \quad \quad \nearrow \quad \searrow \\ R_3P \nearrow \quad \quad \quad \searrow R_3P \\ \quad \quad \quad \nearrow \quad \searrow \\ Br \quad \quad Br \end{array} \right]$. With 2 : 2'-dipyridyl in COMe₂ [(PET₃)₂(CdI₂)₂] yields white *di-iododipyridyl-cadmium*, [dpy CdI₂], which, on account of its lower solubility in H₂O and org. solvents than [dpy HgI₂],

is recommended for use in gravimetric determination of Cd or dipyriddy. Preps. of the following members of this class (*dihalogenobisphosphine-* or *-arsine-μ-dihalogenodcadmium*) are given: $[(PMe_3)_2(CdBr_2)_2]$, m.p. 195–198°; $[(PMe_3)_2(CdI_2)_2]$, m.p. 174–176° (decomp.); $[(PEt_3)_2(CdBr_2)_2]$, m.p. 163–164°; $[(PEt_3)_2(CdI_2)_2]$, m.p. 141°, which in EtOH is an equilibrium mixture $[(PEt_3)_2(CdI_2)_2] \rightleftharpoons [(PEt_3)_2CdI_2] + CdI_2$; $[(PPr^a)_2(CdBr_2)_2]$, m.p. 105–106°; $[(PPr^a)_2(CdI_2)_2]$, m.p. 123–125°; $[(AsEt_3)_2(CdBr_2)_2]$, m.p. 175–178° (decomp.); $[(AsEt_3)_2(CdI_2)_2]$, m.p. 80–81° (decomp.); $[(AsPr^a)_2(CdI_2)_2]$, m.p. 114–116°. Crystallographic data are given for $[(PEt_3)_2(CdBr_2)_2]$, $[(PPr^a)_2(CdI_2)_2]$, and $[(AsPr^a)_2(CdI_2)_2]$; all are monoclinic and isomorphous. X-Ray examination of $[(PEt_3)_2(CdBr_2)_2]$ indicates that the crystals belong to the holohedral class $2/m$ of the monoclinic system; space-group $P2_1/a$, 2 mols. per unit cell. Compounds of class 3 are prepared by interaction of CdX_2 with appropriate members of class 1, or by interaction of appropriate members of classes 1 and 2 (2:1 mol.). These compounds are stable when solid but dissociate in org. solvents, from which, however, they can be recrystallised unchanged; they appear to be of new structural type, probably

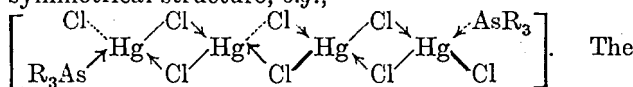


Compounds of this class are easily decomposed by dipyriddy, giving $[dpy CdX_2]$, unlike the analogous class E Hg^{II} compounds. The representative members of this class (*tetrahalogenotrisphosphinedicadmium*) which have been prepared are: $[(PPr^a)_3(CdBr_2)_2]$, m.p. 126–128°; $[(PBu^a)_3(CdBr_2)_2]$, m.p. 93–94.5°; $[(PBu^a)_3(CdI_2)_2]$, m.p. 100–101°. The two tetrahalobromides of this class have orthorhombic crystals showing perfect cleavage parallel to $\{001\}$ and 4 mols. per unit cell. The space-group of the PBu^a_3 derivative is $P2_12_12_1$, which indicates that the mol. need not possess any intrinsic symmetry. It is, however, not an intimate lattice compound of $[(PBu^a)_3CdBr_2]$ and $[(PBu^a)_2(CdBr_2)_2]$ as might be deduced from its mode of prep. Class A of the Hg^{II} derivatives are prepared by analogous methods to class 1 of the Cd compounds; they have the same structure and differ only in that it has been impossible to prepare trialkylphosphine (or -arsine) derivatives. Class A members (*dihalogenobis-phosphine-* or *-arsine-mercury*) prepared are: $[(PPh_3)_2(HgCl_2)_2]$, m.p. 273°; $[(PPh_3)_2(HgI_2)_2]$, m.p. ~250°; $[(AsPh_3)_2(HgBr_2)_2]$, m.p. 182–212°; $[(AsPh_3)_2(HgI_2)_2]$, m.p. 197°. Class B of the Hg^{II} compounds resemble class 2 of the Cd derivatives in prep. and in possessing the tetrahedral "bridged" *trans*-symmetric structure. The following members (*dihalogenobis-phosphine-* or *-arsine-μ-dihalogenodimercury*) have been prepared and studied: $[(PEt_3)_2(HgBr_2)_2]$, m.p. 106°; $[(PEt_3)_2(HgI_2)_2]$, m.p. 121–123°; $[(PPr^a)_2(HgBr_2)_2]$, m.p. 133°; $[(PPr^a)_2(HgI_2)_2]$, α-form, white blunt-ended needles, m.p. 114–115°, β-form, yellow but turning white at 104–107° and having m.p. 113–115° either alone or mixed with α-form; the α-form is converted at room temp. in the solid state or in org. solvent into opaque yellow

β-form; $[(PBu^a)_2(HgBr_2)_2]$, m.p. 116°; $[(PBu^a)_2(HgI_2)_2]$, pale yellow, m.p. 84–85° yields, with dipyriddy in $COMe_2$, $[dpy HgI_2]$; $[(P(n-C_5H_{11}))_2(HgI_2)_2]$, m.p. 54–55°; $[(PPh_3)_2(HgCl_2)_2]$, m.p. 306–309°; $[(PPh_3)_2(HgBr_2)_2]$, m.p. 240–250° (decomp.); $[(AsEt_3)_2(HgCl_2)_2]$, m.p. 162–163°; $[(AsEt_3)_2(HgI_2)_2]$, m.p. 87–88°; $[(AsPr^a)_2(HgBr_2)_2]$, m.p. 91–92°; $[(AsPr^a)_2(HgI_2)_2]$, m.p. 107–108°; $[(AsBu^a)_2(HgBr_2)_2]$, m.p. 86–87°; $[(AsBu^a)_2(HgI_2)_2]$, m.p. 55–56°; $[(AsPh_3)_2(HgCl_2)_2]$, m.p. 251–253°; $[(AsPh_3)_2(HgBr_2)_2]$, m.p. 219°. From crystallographic data on $[(AsEt_3)_2(HgI_2)_2]$, $[(PPr^a)_2(HgBr_2)_2]$, and $[(AsPr^a)_2(HgI_2)_2]$ it is concluded that, unlike the class 2 Cd derivatives, the Hg^{II} compounds are morphologically different. $[(AsPr^a)_2(HgI_2)_2]$ and $[(AsPr^a)_2(CdI_2)_2]$ are isomorphous and have approx. identical cell dimensions. The space-group is $P2_1/a$. Hg^{II} derivatives of class C (*bisphosphine(arsine)trimercuric halide*), prepared by the interaction of the appropriate class B derivative and HgX_2 in hot EtOH or $COMe_2$ solution, are: $[(PEt_3)_2(HgBr_2)_3]$, m.p. 130°; $[(PEt_3)_2(HgI_2)_3]$, m.p. 109–110°; $[(PPr^a)_2(HgCl_2)_3]$, m.p. 113–114°; $[(PBu^a)_2(HgCl_2)_3]$, m.p. 72–74°; $[(AsEt_3)_2(HgI_2)_3]$, m.p. 114–115°; $[(AsPr^a)_2(HgCl_2)_3]$, m.p. 105°; $[(AsBu^a)_2(HgBr_2)_3]$, m.p. 62–64°; $[(AsBu^a)_2(HgI_2)_3]$, m.p. 63–65°. Crystallographic analysis indicates that these are two distinct structures in compounds of this class. $[(AsEt_3)_2(HgI_2)_3]$ forms orthorhombic crystals and there are 4 mols. per unit cell structurally arranged to give a non-centro-symmetrical mol.,



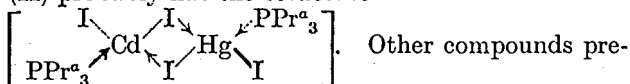
other two compounds examined, $[(AsPr^a)_2(HgCl_2)_3]$ and $[(AsBu^a)_2(HgBr_2)_3]$, have colourless, isomorphous monoclinic crystals and possess a centre of symmetry, space-group $P2_1/a$, 2 mols. per unit cell, the whole forming a bridged mol., e.g., $[(Bu^a_3As)BrHgBr_2HgBr(Bu^a_3As)]$, for which a complete analysis has been carried out and interat. distances and valency angles are given. Mols. of class D (*bisphosphine(arsine)tetrakismercuric halide*) have 2 mols. per unit cell and space-group $P2_1/c$ or $P2_1/m$. Crystallographic data are incomplete but it is almost certain that these mols. have a tetrahedral symmetrical structure, e.g.,



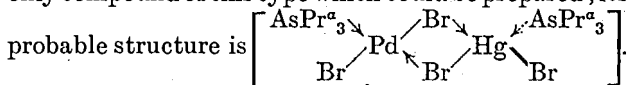
prep. of the following members of this class is given: $[(PEt_3)_2(HgCl_4)_4]$, m.p. 163–164°; $[(PEt_3)_2(HgBr_2)_4]$, m.p. 149–151°; $[(AsEt_3)_2(HgCl_2)_4]$, $COMe_2$, m.p. 112–114°; $[(AsEt_3)_2(HgCl_2)_4]$, prisms, m.p. 138°. I-derivatives could not be prepared. On the other hand, only I-derivatives of class E (*tetrahalogenotris-phosphine-* or *-arsine-dimercury*) could be prepared, usually by the interaction of HgI_2 in aq. KI with excess of phosphine (or arsine). These compounds closely resemble class 3 Cd compounds but are extremely stable to 2:2'-dipyriddy. The following have been prepared: $[(PPr^a)_3(HgI_2)_2]$, m.p. 124–125°; $[(PBu^a)_3(HgI_2)_2]$, m.p. 102°; $[(AsEt_3)_3(HgI_2)_2]$, m.p. 58–70°; $[(AsPr^a)_3(HgI_2)_2]$, m.p. 84–85.5°; $[(AsBu^a)_3(HgI_2)_2]$, m.p. 74–75°.

The stability and inter-relations of the various classes are discussed. Under analogous conditions of prep. ZnX_2 forms no compounds with P(As)R_3 in H_2O but some reaction occurs in EtOH .

XII. When $[(\text{PPr}^{\text{a}})_3\text{CdI}_2]$ (I) is boiled with 1 mol. of HgI_2 in EtOH $[(\text{PPr}^{\text{a}})_3\text{CdHgI}_4]$ (II), *di-iodobis(tri-n-propylphosphine)-μ-di-iodocadmium-mercury*, m.p. 141°, is formed. (II) is also formed from $[(\text{PPr}^{\text{a}})_3\text{CdI}_4]$ and $[(\text{PPr}^{\text{a}})_3\text{HgI}_4]$, indicating that both parent substances must be dissociated in hot EtOH to $\text{PPr}^{\text{a}}_3 \rightarrow \text{CdI}_2$ and $\text{PPr}^{\text{a}}_3 \rightarrow \text{HgI}_2$ radicals. (II) probably has the structure

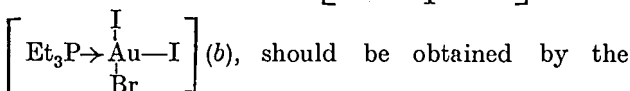
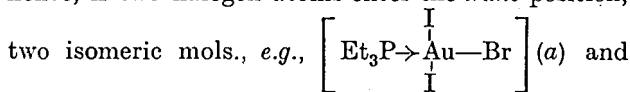


pared are: $[(\text{PBu}^{\text{a}})_3\text{CdHgI}_4]$, m.p. 140—141°; $[(\text{n-C}_5\text{H}_{11})\text{Cd}(\text{PPr}^{\text{a}})_3\text{HgI}_4]$, m.p. 91—93°; $[(\text{PPr}^{\text{a}})_3\text{CdHgBr}_4]$, m.p. 179°; $[(\text{PPr}^{\text{a}})_3\text{CdHgBr}_2\text{I}_2]$, needles, m.p. 138°; $[\text{AsPr}^{\text{a}}_3(\text{PPr}^{\text{a}})_3\text{CdHgI}_4]$, m.p. 121—123°. *Dibromobis(tri-n-propylarsine)-μ-dibromopalladium-mercury* was obtained as orange crystals, m.p. 89—90°, by boiling equiv. quantities of $[(\text{AsPr}^{\text{a}})_3\text{PdBr}_2]$ and HgBr_2 in EtOH . This was the only compound of this type which could be prepared; its



No reaction occurred between $[(\text{PBu}^{\text{a}})_3\text{PdI}_2]$ and HgI_2 . $[(\text{PPr}^{\text{a}})_3\text{PdCl}_2]$ and HgCl_2 gave $[(\text{PPr}^{\text{a}})_3(\text{PdCl}_2)_2]$ and $[(\text{PPr}^{\text{a}})_3(\text{HgCl}_2)_2]$. $[(\text{PEt}_3)_2\text{PdCl}_2]$ and HgCl_2 gave $[(\text{PEt}_3)_2(\text{PdCl}_2)_2]$ and $[(\text{PEt}_3)_2(\text{HgCl}_2)_4]$. $[(\text{PBu}^{\text{a}})_3(\text{PdI}_2)_2]$ and $[(\text{PBu}^{\text{a}})_3(\text{HgI}_2)_2]$ gave $[(\text{PBu}^{\text{a}})_3\text{PdI}_2]$ and HgI_2 . Pd—Cd compounds could not be prepared nor were bridged $\text{Cu}^{\text{I}}(\text{Ag})\text{—Hg}^{\text{II}}$ compounds formed by the interaction of HgI_2 and $[\text{P(As)R}_3\text{Cu(Ag)I}_4]$. By adding PPr^{a}_3 (3 mols.) to AgI (1 mol.) and HgI_2 (1 mol.) in aq. KI, followed by vigorous shaking, white needles of *di-iodobis(tri-n-propylphosphine)mercury*, $[(\text{PPr}^{\text{a}})_3\text{HgI}_2]$, m.p. 117—119°, were obtained.

XIII. 2-Covalent Au^{I} compounds readily combine with 1 mol. of a halogen to give 4-covalent Au^{III} compounds. The Au^{I} compounds are linear and hence, if two halogen atoms enter the *trans*-position,



action of I on $[\text{Et}_3\text{P} \rightarrow \text{AuBr}]$ or by the action of IBr on $[\text{Et}_3\text{P} \rightarrow \text{AuI}]$. From the fact that in all such mixed halogen Au^{III} complexes only one form is encountered it is concluded that the groups around the 4-covalent Au atom possess considerable mobility and only the more stable isomeride occurs. The relative stabilities of the trihalogeno-derivatives is discussed. Attempts to introduce acid radicals other than halides into the Au^{III} complex have failed. The Au^{III} are readily reduced to Au^{I} by passing SO_2 into their EtOH solutions at room temp. and the more electronegative halogen atoms are preferentially removed; e.g., with SO_2 $[\text{PEt}_3\text{AuCl}_2\text{I}]$ gave $[\text{PEt}_3\text{AuI}]$ and with COMe_2 $[\text{PEt}_3\text{AuClBrI}]$ gave $[\text{PEt}_3\text{AuI}]$.

Preps. of the following compounds are given: Au compounds, *monobromo(trimethylphosphine)gold*, $[\text{PMe}_3\text{AuBr}]$, m.p. 225° (decomp.); *monobromo(triethylphosphine)gold*, $[\text{PET}_3\text{AuBr}]$, m.p. 87°. (A corr. val. for the m.p. of $[\text{PET}_3\text{AuCl}]$ is given as 84—85°.) Au^{III} compounds, *trihalogeno(triphenylphosphine)gold*, $[\text{PMe}_3\text{AuBr}_3]$, m.p. 162°; $[\text{PET}_3\text{AuCl}_3]$, m.p. 121°; $[\text{PEt}_3\text{AuCl}_2\text{Br}]$, m.p. 119—120°; $[\text{PEt}_3\text{AuClBr}_2]$, m.p. 128—129°; $[\text{PEt}_3\text{AuBr}_3]$, m.p. 129°; $[\text{PEt}_3\text{AuCl}_2\text{I}]$, m.p. 105—106°; $[\text{PEt}_3\text{AuClBrI}]$, m.p. 107—108°; $[\text{PEt}_3\text{AuBr}_2\text{I}]$, m.p. 109°; $[\text{PEt}_3\text{AuClI}_2]$, m.p. 94—95°; $[\text{PEt}_3\text{AuBrI}_2]$, m.p. 90—91°; $[\text{PEt}_3\text{AuI}_3]$, m.p. 77°; $[\text{PPr}^{\text{a}}_3\text{AuClBr}_2]$, m.p. 145°. *Toluene-3:4-bis(thiotriethylphosphine gold)*, m.p. 124—125°, has also been prepared.

W. R. A.

Methylboric acid and its anhydride. **Methylboron fluorides.** A. B. BURG (J. Amer. Chem. Soc., 1940, 62, 2228—2234).— Me_3BO_3 and MgMeI give impure *methylboric acid* (I) (cf. Khotinsky *et al.*, A., 1909, i, 864; Snyder *et al.*, A., 1938, II, 87), which by repeated passage over < the calc. amount of partly dehydrated gypsum gives trimeric *methylboric anhydride* [*trimethyltriborine trioxan*] (II), $(\text{MeBO})_3$, m.p. —38° (vac.), b.p. 79° (extrapolated from the v.p.). (II) is analysed by oxidation by $\text{Cl}_2\text{—H}_2\text{O}$ at 100° to H_3BO_3 and by HNO_3 at 300° to CO_2 and H_3BO_3 . Its vapour deviates from the perfect gas laws at room temp. It is strongly adsorbed by all drying agents, least by CaSO_4 . When treated with < 1 mol. of H_2O and then fractionated, it gives pure (I), m.p. indef., 73—77° or 95—100° (vac.), for which v.p. are determined. Dissociation of the vapour of (I) agrees with the reaction, $3\text{MeB(OH)}_2 \rightleftharpoons (\text{MeBO})_3 + 3\text{H}_2\text{O}$, for which $\Delta H = 9300$ g.-cal. and $\Delta F^\circ = 9300 - 22.31T$. The stable compounds, $(\text{MeBO})_3\text{NH}_3$ (III) and $(\text{MeBO})_3\text{NMe}_3$, and the unstable compound, $(\text{MeBO})_3\text{2NH}_3$ (IV), are prepared, but $(\text{MeBO})_3\text{3NH}_3$ does not exist. V.p. of these compounds and the dissociation of (III) are recorded. BF_3 and (II) give high yields of *B Me difluoride*, BMeF_2 , m.p. —130.5°, b.p. —62.3°. $(\text{Me}_2\text{B})_2\text{O}$ and BF_3 give similarly *B Me₂ fluoride*, BMe_2F , m.p. —147.4°, b.p. —42.2°. Cyclic structures are assigned to (II), (III), and (IV), the 2 NH_3 of (IV) being united as $\text{B} \leftarrow \text{NH}_3 \leftarrow \text{NH}_3$.

R. S. C.

Grignard reagent. M. KILPATRICK and E. A. BARR, jun. (J. Amer. Chem. Soc., 1940, 62, 2242).—The black ppt. obtained from Mg and org. halides is colloidal Mg.

R. S. C.

Dehydration of certain homologues of cyclopentanol. III. J. I. DENISENKO and A. D. NABER (J. Gen. Chem. Russ., 1940, 10, 193—201).—1- δ -Phenylbutylcyclopentanol and anhyd. $\text{H}_2\text{C}_2\text{O}_4$ (2 hr. at 130—135°) give 1- δ -phenylbutyl- Δ^1 -cyclopentane (I) in 85% yield. With P_2O_5 or conc. H_2SO_4 the product is 1-cyclopentyl-1:2:3:4-tetrahydronaphthalene, b.p. 140—141°/3 mm., also obtained from (I) and H_2SO_4 .

R. T.

Isolation of carotene from green plant tissue.—See A., 1940, III, 944.

Molecular compounds of aromatic hydrocarbons with nitro-compounds and with anti-mony trihalides.—See A., 1940, I, 412.

Synthesis and properties of mono-*n*-alkylbenzenes. I. Alkylation of benzene. G. SHEN, T. Y. JU, and C. E. WOOD (J. Inst. Petroleum, 1940, 26, 475—487).—The efficacy of seven methods for synthesising higher *n*-alkylbenzenes is considered. The best is the reduction (Pd or Clemmensen) of ketones obtained by the Friedel-Crafts reaction.

A. LI.

4-Phenylcyclohexene. C. C. PRICE and J. V. KARABINOS (J. Amer. Chem. Soc., 1940, 26, 2243).—4-Phenylcyclohexene, prepared from CH_3CHPh and $(\text{CH}_3\text{CH})_2$ (cf. Alder *et al.*, A., 1938, II, 131), has b.p. 88—90°/16 mm., n_D^{20} 1.5420, d_4^{20} 0.9715. This confirms the structure of the 3-isomeride (A., 1940, II, 276).

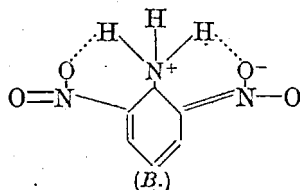
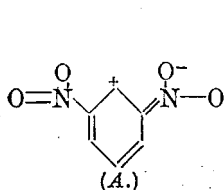
R. S. C.

Rate of nitration of benzene.—See B., 1940, 724.

s-Tri-*p*-tolylbenzene. T. R. SAMPEY (J. Amer. Chem. Soc., 1940, 62, 1953).— $\text{s-C}_6\text{H}_3(\text{C}_6\text{H}_4\text{Me-}p)_3$, m.p. 170—171°, is best (67—70%) prepared by heating $p\text{-C}_6\text{H}_4\text{Me-COMe}$ (10 g.) with KHSO_4 (2 g.) or conc. H_2SO_4 (0.2—0.3 c.c.) and $\text{K}_2\text{S}_2\text{O}_7$ (2 g.) at 190° for 6 hr.

R. S. C.

Acidity of aromatic nitro-compounds towards amines. Effect of double chelation. G. N. LEWIS and G. T. SEABORG (J. Amer. Chem. Soc., 1940, 62, 2122—2124).—Colours developed by aromatic polynitro-hydrocarbons and NH_3 or amines (not



alkali hydroxides) are interpreted as due to addition to the resonance form (type A) to give doubly chelated compounds of type (B). This is supported by the effects of substitution in either component.

R. S. C.

Presence of indole in "practical" α -methyl-naphthalene. M. S. KHARASCH, S. S. KANE, and H. C. BROWN (J. Amer. Chem. Soc., 1940, 62, 2242—2243).—"Practical" $\alpha\text{-C}_{10}\text{H}_7\text{Me}$ is shown to contain 1—2% of indole by condensation with $(\text{COCl})_2$ to give 3-indolylglyoxalyl chloride. Pure $1\text{-C}_{10}\text{H}_7\text{Me}$ does not discolour in air.

R. S. C.

Organic molecular compounds.—See A., 1940, I, 436.

Preparation of 1:5-dimethylnaphthalene. (Miss) E. W. J. BURZ (J. Amer. Chem. Soc., 1940, 62, 2557).—1-Keto-5-methyl-1:2:3:4-tetrahydronaphthalene is obtained from $o\text{-C}_6\text{H}_4\text{MeBr}$ in six stages, no separation of isomerides being required at any stage. With MgMeI it gives a carbinol, dehydrated by I-CO_2 at 200° to a mixture which with Pd-C at 250° gives 1:5- $\text{C}_{10}\text{H}_6\text{Me}_2$, m.p. 80° (picrate, m.p. 137°).

R. S. C.

Methyl and dimethyl derivatives of cholanthrene. L. F. FIESER and D. M. BOWEN (J. Amer. Chem. Soc., 1940, 62, 2103—2108).—Prep. of 1:4- $\text{C}_{10}\text{H}_6\text{Me-SO}_3\text{K}$ and thence of 1:4- $\text{C}_{10}\text{H}_6\text{MeBr}$ is modified. The derived Grignard reagent with 4-cyano-

hydrindene (I) in boiling $\text{Et}_2\text{O-C}_6\text{H}_6\text{-N}_2$ gives a ketimine hydrochloride, hydrolysed by conc. HCl-AcOH-PhMe to 4:4'-methyl-1-naphthoylhydrindene (85%), m.p. 84.6—85.1°, which at 400—410° gives a difficultly separable mixture of 6-methylcholanthrene (24%), m.p. 204.2—205.2° (picrate, m.p. 208.4—209°), and (?) cholanthrene. 4-Cyano-7-methylhydrindene gives similarly 4:4'-methyl-1'-naphthoyl-7-methylhydrindene (81%), m.p. 130.2—131.2°, b.p. 230°/1 mm., and 6:20-dimethylcholanthrene (30%), m.p. 175.8—176.5° (picrate, m.p. 199.8—200.2°). The preps., $p\text{-C}_6\text{H}_4\text{Me-NHAc} \rightarrow 1:3:4\text{-C}_6\text{H}_2\text{MeCl-NHAc} \rightarrow 1:3:4\text{-C}_6\text{H}_2\text{MeCl-NH}_2 \rightarrow 1:3:4\text{-C}_6\text{H}_2\text{MeCl-MgBr}$ and CH(OEt)_3 in Et_2O give an aldehyde, which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and $\text{C}_5\text{H}_5\text{N}$ at 100° yield 2-chloro-4-methylcinnamic acid (21%), m.p. 223.7—224°. 2% Na-Hg then gives β -3-chloro-p-tolylpropionic acid, m.p. 96.6—97.4°, which with $\text{PCl}_5\text{-C}_6\text{H}_6$ and then $\text{AlCl}_3\text{-CS}_2$ at 0° (later 30°) yields 4-chloro-6-methylhydrind-1-one (95%), m.p. 104—104.5°. This is reduced (Clemmensen) to 4-chloro-6-methylhydrindene, b.p. 128—132°/27 mm., converted by $\text{CuCN-C}_5\text{H}_5\text{N-MeCN}$ at 240—250° into 4-cyano-6-methylhydrindene (61%), b.p. 138—139°/10 mm., which with conc. HCl at 180—200° gives 6-methylhydrindene-4-carboxylic acid, m.p. 158.6—159.3°, or with $1\text{-C}_{10}\text{H}_7\text{-MgBr}$ gives 4:1'-naphthoyl-6-methylhydrindene (94%), b.p. 205—210°/1.5 mm., and thence 22-methylcholanthrene (27%), m.p. 154.5—155° (picrate, m.p. 173.6—174°). 4:4'-Methyl-1'-naphthoylhydrindene (89%), b.p. 230°/1.5 mm., and 6:22-dimethylcholanthrene (23%), m.p. 161.7—162.4° (picrate, m.p. 185.6—186°), are similarly obtained. Preps. of 8-chloro-1-bromo- and thence of 8-chloro-1-methylnaphthalene (II) are improved. With $\text{CuCN-C}_5\text{H}_5\text{N-MeCN}$ at 240°, (II) gives 1-cyano-8-methylnaphthalene (III) (79%), m.p. 95—95.5°, hydrolysed by boiling KOH-aq. EtOH to 8-methyl-1-naphthoamide, m.p. 208.7—209.4° (could not be converted into the acid). The Li derivative from (II) with (I) gives a ketimine hydrochloride (37%), which resists hydrolysis. The Mg derivative from 7-bromo-4-methylhydrindene (modified prep.) with (III) in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ gives 8-methyl-1-naphthyl 7-methyl-4-hydrindenzyl ketimine hydrochloride (29%), cryst., which resists hydrolysis. M.p. are corr.

R. S. C.

Synthesis of 1'-methyl-1:2-benzanthracene and 5-methylchrysene. W. E. BACHMANN and R. O. EGERTON (J. Amer. Chem. Soc., 1940, 62, 2250—2253).—4-Methylphenanthrene, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 at -15° give γ -keto- γ -5-methyl-3-phenanthryl-*n*-butyric acid (I), m.p. 195—196.5°, also obtained from 3-acetyl-5-methylphenanthrene by bromination (the $3\text{-CH}_2\text{Br-CO}$ compound melts at 105—107°), condensation with $\text{CH}_2(\text{CO}_2\text{Et})_2$, etc. $\text{Zn-Hg-HCl-AcOH-PhMe}$ then gives γ -5-methyl-3-phenanthryl-*n*-butyric acid, m.p. 92—94°, which with $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N-Et}_2\text{O}$, followed by $\text{SnCl}_4\text{-C}_6\text{H}_6$, gives 5-keto-1'-methyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 153.5—154.5°. Reduction (as above) thereof gives 1'-methyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 83.5—84.5° (picrate, m.p. 140.5—142°), dehydrogenated by Pd-C at 300—320° to 1'-methyl-1:2-benzanthracene. 1-Bromoacetyl-4-

methylphenanthrene (prep. from the 1-Ac derivative), m.p. 80–82°, gives γ -keto- γ -4-methyl-1-phenanthryl-*n*-butyric acid, m.p. 133–136°, reduced to γ -4-methyl-1-phenanthryl-*n*-butyric acid (II), m.p. 152–152.5°, also obtained by reduction of the mother-liquors from (I). 1-Keto-4-methyl-1:2:3:4-tetrahydrophenanthrene, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$, Zn, and a trace of I in $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ give an ester, which by hydrolysis (cold, dil. HCl) and dehydrogenation (Pd-C; 240–260°) yields 4-methyl-1-phenanthrylacetic acid, m.p. 188–189°. By the Arndt-Eistert procedure this affords successively β -4-methyl-1-phenanthrylpropionic acid, m.p. 155–156°, and (II). Cyclisation of (II) as above yields 1-keto-11-methyl-1:2:3:4-tetrahydrochrysene, m.p. 139.5–140.5°, reduced to 11-methyl-1:2:3:4-tetrahydrochrysene, m.p. 71–72° (picrate, m.p. 141–142°), which with Pd-C at 300–320° gives 5-methylchrysene, new m.p. 118–118.8° (corr.) [picrate, m.p. 141–142° (corr.)]; *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 171–173°. 1- and 3-Methylchrysene have m.p. 256.5–257° (corr.) and 172.5–173° (corr.), respectively. R. S. C.

Polycyclic aromatic hydrocarbons. XXV. 1- and 2-Alkyl derivatives of 3:4-benzphenanthrene. J. L. EVERETT and C. L. HEWETT (J.C.S., 1940, 1159–1162).—3:4-Benz-1-phenanthroyl chloride (cf. Hewett, A., 1940, II, 212) gives 3:4-benz-1-phenanthramide, m.p. 238–239°, which with MgMeI , followed by hydrolysis (conc. HCl-AcOH), yields 1-acetyl-3:4-benzphenanthrene, m.p. 95–96°, b.p. 227°/0.5 mm., the semicarbazone, m.p. 180° (decomp.), of which with NaOEt at 180° (18 hr.) gives 1-ethyl-3:4-benzphenanthrene, m.p. 66–67°, b.p. 200°(bath)/0.5 mm. (picrate, m.p. 116–117°). The following are prepared similarly: 1-propionyl-, m.p. 94.5–95° (semicarbazone, m.p. 229–230°), and 1-*n*-propyl-3:4-benzphenanthrene, m.p. 67–68° (picrate, m.p. 93–94°). *Me* 3:4-benz-1-phenanthroate, m.p. 96.5–97.5° (the *Et* ester, m.p. 81–82°, gives poor results), with MgMeI followed by NH_4Cl -ice and picric acid yields the picrate, m.p. 94–95°, of 1-isopropenyl-, hydrogenated (Pd) to 1-isopropyl-3:4-benzphenanthrene, m.p. 76–77° [picrate, $2\text{C}_{21}\text{H}_{18}, 3\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m.p. 105–106°; compound, m.p. 112.5–113°, with $\text{C}_6\text{H}_3(\text{NO}_2)_3$]. 3:4-Benz-2-phenanthroic acid (*loc. cit.*) gives the corresponding chloride, m.p. 110–111°, and the amide (I), m.p. 228–229°, which with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ or with MgMeI yields the nitrile, m.p. 128–129°, subliming 150°/0.7 mm. With MgMeI followed by hydrolysis, (I) gives 2-acetyl-, m.p. 111.5–112.5° (semicarbazone, m.p. 235–236°), converted as before into 2-ethyl-3:4-benzphenanthrene, new m.p. 67–68° (picrate, new m.p. 83–84°). Similarly the semicarbazone, m.p. 211–212°, of 2-propionyl-, m.p. 115.5–116.5°, b.p. 230–234°/0.4 mm., gives 2-*n*-propyl-3:4-benzphenanthrene, m.p. 71.5–72.5° (picrate, m.p. 103.5–104°). 3:4-Benz-2-phenanthranilide, m.p. 214–215°, in $\text{C}_2\text{H}_2\text{Cl}_4$ with PCl_5 followed by $\text{SnCl}_2\text{--Et}_2\text{O--HCl}$ gives 3:4-benz-2-phenanthraldehyde, m.p. 130.5–131.5°, b.p. 260°(bath)/0.4 mm. (semicarbazone, m.p. 240–241°), reduced to 2-methyl-3:4-benzphenanthrene. E. W. W.

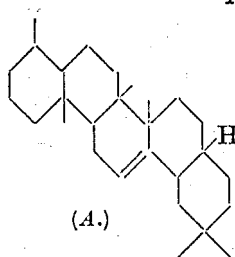
Synthesis of 4:5-dimethylchrysene. M. S. NEWMAN (J. Amer. Chem. Soc., 1940, 62, 2295–2300).—Synthesis of 4:5-dimethylchrysene (I) is

difficult but is achieved by the following reactions, which introduce both Me at an early stage and effect the fourth ring-closure at a distance from their interference. Only the final dehydrogenation gives trouble. Many of the oily products are mixtures of stereoisomerides. $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ and dry $(\text{CH}_2\text{O})_3$ in Et_2O give 62.4% of impure or 42% of pure (f.p. 35.0°, b.p. 109°/12 mm.) *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{OH}$ [phenylurethane, m.p. 79.0–79.6°; obtained also in 55% yield from *o*- $\text{C}_6\text{H}_4\text{MeBr}$ and $(\text{CH}_2\text{O})_3$ in Et_2O] (and $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{OH}$), which with SOCl_2 and a drop of $\text{C}_3\text{H}_5\text{N}$ in C_6H_6 gives 89% of *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Cl}$ (II), b.p. 84°/14 mm., and 11% of a polymeride. NaCN in boiling, aq. EtOH converts (II) into *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CN}$ (III) (86%), b.p. 225.5°/14 mm. $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{OH}$ (prep. from MgPhBr and propylene oxide in boiling Et_2O), b.p. 105.5–107°/14–15 mm. (phenylurethane, m.p. 88.2–88.8°), with $\text{PBr}_3\text{--C}_6\text{H}_6$, first at room temp. and later boiling, or with 48% HBr gives $\text{CH}_2\text{Ph}\cdot\text{CHMeBr}$ (IV), b.p. 112.5–114°/20–21 mm., the structure of which is proved by conversion of the derived Grignard reagent by CO_2 into $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, b.p. 172–173°/23 mm. (amide, m.p. 106–107°). (III), (IV), and NaNH_2 give γ -phenyl- α -*o*-tolylisovaleronitrile (63%), b.p. 159–160°/1 mm., hydrolysed by alkali at 150° only to the amide, m.p. 115–122°, but by boiling 6:8:47 (vol.) $\text{H}_2\text{O--H}_2\text{SO}_4\text{--AcOH}$ (62 hr.) to the crude oily acid (88% with 6.6% of amide). $\text{PCl}_5\text{--C}_6\text{H}_6$, followed by $\text{AlCl}_3\text{--C}_6\text{H}_6$, then gives 1-keto-2-*o*-tolyl-3-methyl-1:2:3:4-tetrahydronaphthalene (92%), b.p. 170°/0.5–1 mm., converted by Zn, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$, and a little I in C_6H_6 into an ester, which by dehydrogenation and hydrolysis gives 2-*o*-tolyl-3-methyl-3:4-dihydro-1-naphthylacetic acid (V) (17.7%), m.p. 180–182°, and liquid isomerides (VI) (34.3%), b.p. 215–223°/7–8 mm. Hydrogenation of (V) gives an oily H_4 -acid, which with, successively, $\text{PCl}_5\text{--C}_6\text{H}_6$, $\text{AlCl}_3\text{--C}_6\text{H}_6$, $\text{Al}(\text{OPr}^\beta)_3\text{--Pr}^\beta\text{OH}$, and S at 230° gives (I), m.p. 164.0–164.8° [*s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 131–132°; picrate unobtainable]. No (I) is obtained from (VI). The chrysene structure of (I) is proved by absorption max. at 2740 ($\log \epsilon$ 5.11) and 3440 Å. ($\log \epsilon$ 4.34) and a point of inflexion at 3800 Å. ($\log \epsilon$ 2.87). M.p. are corr. R. S. C.

Isolation and identification of fluoranthrene from carbon black. J. REHNER, jun. (J. Amer. Chem. Soc., 1940, 62, 2243–2244).—Isolation of fluoranthrene from commercial “thermatonic C” is described. R. S. C.

Conversion of quillaic acid into a hydrocarbon.

G. A. R. KON and H. R. SOPER (J.C.S., 1940, 1335).—The CO ester obtained by oxidation and reduction of Me quillaate is reduced by hot NaOEt and N_2H_4 , with simultaneous removal of CO_2Me , to norhedro-betulene (A), $\text{C}_{28}\text{H}_{46}$, having m.p. 154°, $[\alpha]_D^{25} +33^\circ$ in hexane. A. LI.



Aromatic amines and 2-fluoro-5- ω -dinitrostyrene. D. E. WORRALL and H. T. WOLOSINSKI (J. Amer. Chem. Soc., 1940, 62, 2449).—F enhances

the addition of bases to $\text{CHAr}:\text{CH}\cdot\text{NO}_2$ less than does Cl, Br, or I. *o*-Fluoro- ω -nitrostyrene (I) (prep. in ~60% yield from $\text{o-C}_6\text{H}_4\text{F}\cdot\text{CHO}$, MeNO_2 , and a little NMe_3), m.p. 56.5—57.5° (ω -Br-derivative, m.p. 89—90°), and fuming HNO_3 give the 5- NO_2 -derivative, m.p. 142—143°. With NH_2Ar this gives α -nitro- β -anilino-, m.p. 134—135°, β -m-, m.p. 105—106°, and β -*p*-toluidino-, m.p. 116—117°, and β -phenylhydrazino-, m.p. 103—104°, β -2-fluoro-5-nitrophenylethane, and with benzidine gives NN' -di-(β -nitro- α -2-fluoro-5-nitrophenylethyl)benzidine, m.p. 139.5—140.5°. $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, NH_2OH , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}_2$, and NH_3 do not react. A compound, $\text{C}_{28}\text{H}_{24}\text{O}_4\text{N}_4\text{F}_2$, m.p. 134—135°, is obtained from benzidine and ? (I). R. S. C.

Condensation of sulphanilamide with an enol. N^4 - α -Bromotetronylsulphanilamide. W. D. KUMLER (J. Amer. Chem. Soc., 1940, 62, 2560—2561).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (I) and α -bromotetronic acid at 110—120° or in boiling AcOH , dioxan, or (best, 31%) PhMe give N^4 - α -bromo- β -tetronylsulphanilamide, a very weak acid, which does not couple, is not toxic (orally) to mice, and equals (I) in efficiency against β -haemolytic streptococci. $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ does not condense. R. S. C.

Quaterphenyl. I. Some dihydroxy-derivatives. J. HARLEY-MASON and F. G. MANN (J.C.S., 1940, 1379—1385).—4'-Iodo-4-methoxydiphenyl and Cu-bronze in N_2 at 280° afford 4:4'''-dimethoxyquaterphenyl (I), m.p. 338—340°, also obtained from 4'-bromo-4-methoxydiphenyl-Mg-EtBr- C_6H_6 at 30° (reaction initiated with EtBr), then anhyd. CuCl_2 (cf. Hey *et al.*, A., 1936, 991). (I) and $\text{CrO}_3\text{-AcOH}$ give diphenyl-4:4'-dicarboxylic acid (II). (I) and HI (d 1.7)- AcOH at 180° (sealed tube) give 4:4'''-dihydroxyquaterphenyl, m.p. 419—422° [purified through the diacetate (III), m.p. 325° (decomp.); di(chloroacetate), decomp. 360° without melting], which has no oestrogenic properties and could not be oxidised to the corresponding quinone [AcOH-CrO_3 gives (II)]. $p\text{-C}_6\text{H}_4\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, new m.p. 212—214° (improved prep.), and Cu-bronze at 235—245° yield 4:4'''-dinitroquaterphenyl, m.p. 317—320°, sublimes at 320°/0.01 mm. (could not be prepared from quaterphenyl), oxidised by $\text{CrO}_3\text{-AcOH}$ to 4-nitrodiphenyl-4'-carboxylic acid, m.p. 338—340°, and reduced by $\text{SnCl}_2\text{-AcOH-HCl}$ (decomp. of the stannichloride by 20% aq. NaOH) to 4:4'''-diaminoquaterphenyl, m.p. 312—315° (partial decomp.), sublimes at 310—320°/0.01 mm. (Ac_2 derivative, m.p. 385°), converted by the diazo-reaction, followed by acetylation, into (III). Diacetylbenzidine (IV)- $\text{Ac}_2\text{O-AcOH}$ at 5° with nitrous fumes give NN' -bisnitrosoacetylbenzidine, explodes at 84—87°, which with excess of PhOMe affords a little (IV) only. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Cl-PhOMe-aq. NaOH}$ give 4'-bromo-2-methoxydiphenyl (V), m.p. 63—64°, b.p. 200—201°/18 mm., and 4-methoxydiphenyl (VI), m.p. 144—145°. $p\text{-C}_6\text{H}_4\text{I}\cdot\text{N}_2\text{Cl}$ similarly affords 4'-iodo-2-methoxydiphenyl (VII), m.p. 61—63°, b.p. 140—143°/0.05 mm., the 4-OMe-isomeride, m.p. 182—183°, and $p\text{-C}_6\text{H}_4\text{I}_2$. Tetrazotised benzidine and an excess of PhOMe give no identifiable product. 4'-Nitro-2-hydroxydiphenyl yields (Ac_2O) 4'-nitro-2-acetoxy-, m.p. 142—145°, and ($\text{Me}_2\text{SO}_4\text{-aq. NaOH}$ at

60°) 2-methoxy-diphenyl, m.p. 62—63°; the latter and reduced Fe-AcOH-70\% EtOH give the 4'- NH_2 -compound (hydrochloride; Ac derivative, m.p. 147—148°) and thence (diazo-reaction) (V) and (VII). (VII) and (V) are converted [as for (I)] into 2:2'''-dimethoxyquaterphenyl (VIII), m.p. 188—191° [oxidised to (II)], whence the 2:2'''-(OH) $_2$ -compound, m.p. 238—240° [oxidised to (II); diacetate, m.p. 221—224°; di(chloroacetate), m.p. 166—169°; di-*o*-nitrobenzoate, m.p. 190—192°]. (V) and (VI), added alternately to $\text{Mg-Et}_2\text{O-EtBr}$ followed by anhyd. CuCl_2 , give (I), (VIII), and 2:4'''-dimethoxy-, m.p. 223—224°, and thence dihydroxy-quaterphenyl, m.p. 268—270° [oxidised to (II); diacetate, m.p. 189—192°; di(chloroacetate), m.p. 158—160°; di-*o*-nitrobenzoate, m.p. 206—208°]. A. T. P.

Aldehyde-resorcinol condensations. J. B. NIEDERL and H. J. VOGEL (J. Amer. Chem. Soc., 1940, 62, 2512—2514).— $m\text{-C}_6\text{H}_4(\text{OH})_2$ and RCHO in 10% H_2SO_4 at 100° give compounds,



$(\text{OH})_2\text{C}_6\text{H}_2<]$, + H_2O , in which $\text{R} = \text{Me}$ and Et , and + $2\text{H}_2\text{O}$, in which $\text{R} = \text{Bu}^2$, all having m.p. >300° (decomp.). These give octa-acetates, m.p. 282° (decomp.), 242° (decomp.), and >300° (decomp.), and -propionates, m.p. 222° (decomp.), 114° (decomp.), and —, and Me_3 ethers (prep. by Me_2SO_4 and 30% NaOH), + H_2O , m.p. 256° (decomp.), 227° (decomp.), and —, respectively. R. S. C.

Aralkyl ethers of phenols.—See B., 1940, 781, 782.

Hexaestrol [4:4'-dihydroxy- $\gamma\delta$ -diphenylhexane]. W. F. SHORT (Chem. and Ind., 1940, 703).—The prep. of hexaestrol Me_2 ether from Mg and anethole hydrobromide (Docken *et al.*, A., 1940, II, 342) has been previously patented (B.P. 523,320, B., 1940, 701). H. W.

Crystalline vitamin-A palmitate and vitamin-A alcohol. J. G. BAXTER and C. D. ROBESON (Science, 1940, 92, 203—204).—The prep. of vitamin-A alcohol (I), new m.p. 63—64° (cf. A., 1939, III, 601), from rich fish-liver oils is described. The average extinction coeff. at 328 $\text{m}\mu$. of 18 preps. is 1725, whilst that calc. from the blue val. is 1700. The extinction coeff. of the (I)- SbCl_3 blue colour is 4700 at 622 $\text{m}\mu$. Palmityl chloride, (I), and quinoline in CHCl_3 at -15° give the palmitate (II), m.p. 26—28°, which has an average extinction coeff. of 940, whilst that calc. from the blue val. is 933 at 328 $\text{m}\mu$. The extinction coeff. of the (II)- SbCl_3 blue colour is 2490 at 620 $\text{m}\mu$. The distilled esters from a fish-liver oil, vitamin-A β -naphthoate, (II), and β -carotene are equally stable in refined cottonseed oil when exposed at comparable concns. to air in the dark. The potency of (I) is $>2.7 \times 10^6$ U.S.P. units per g. L. S. T.

Synthesis of γ -4-hydroxycyclohexyl-*n*-propyl alcohol, a product of the hydrogenation of lignin. E. BOWDEN and H. ADKINS (J. Amer. Chem. Soc., 1940, 62, 2422—2423).— $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ [prep. in 82% yield from $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I), EtOAc , and Na at <0°], m.p. 48—50°, b.p. 132°/1 mm., with $\text{H}_2\text{-Raney Ni}$ in EtOH

at 80—90°/100 atm. gives p -OMe·C₆H₄·[CH₂]₂·CO₂Et, b.p. 103°/0.1 mm., converted by HI (d 1.7) into p -OH·C₆H₄·[CH₂]₂·CO₂H (II), m.p. 128—129°, also obtained less well from (I), CH₂(CO₂Et)₂, and piperidine etc. The Et ester, b.p. 140°/0.2 mm., of (II), prepared by H₂SO₄-EtOH, is hydrogenated (Raney Ni; EtOH; 175—200°/150 atm.) to *Et* β -4-hydroxycyclohexylpropionate, b.p. 102—103°/0.2 mm., which with H₂-Cu chromite in EtOH at 250°/200 atm. gives γ -4-hydroxycyclohexyl-*n*-propyl alcohol (93%), b.p. 125—127°/1 mm. (cf. A., 1938, II, 332), identified by oxidation to the 4-CO-acid, m.p. 60—65° (2:4-dinitrophenylhydrazones, m.p. 125—127°, which in hot EtOH gives the derivative, m.p. 90—94°, of the Et ester). *Et* p -methoxybenzylmalonate has b.p. 138°/0.1 mm. R. S. C.

Action of magnesium phenyl bromide on anthraquinones. C. F. H. ALLEN and A. BELL (J. Amer. Chem. Soc., 1940, 62, 2408—2412; cf. A., 1938, II, 147).—Good yields of 9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracenes are obtained from the appropriate anthraquinones and MgPhBr in Bu₂O. 9:10-Dihydroxy-2:9:10-triphenyl-, m.p. 203°, -9:10-diphenyl-2:3-dimethyl-, m.p. 227°, -2:3:9:10-tetraphenyl-, m.p. 294°, and -9:10-diphenyl-1:2-tetramethylene- (I), m.p. 226°, -9:10-dihydroanthracene are thus prepared. In the naphthacene series diols and diketones (formed by a 1:4-addition of MgPhBr) are formed if Mg is absent, but presence of Mg and thus of Mg + MgBr₂ leads to their gradual decomp. by heat to hydrocarbons; in this series PhMe is preferable to Bu₂O as solvent. Heating (I) at 150° gives 45% of 9:10-diphenyl-1:2-tetramethylenanthracene, m.p. 295°. R. S. C.

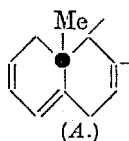
Free radicals and radical stability. XI. Methyltriphenylmethyls. S. T. BOWDEN and T. L. THOMAS. **XII. Fluorotriphenylmethyl and the reactivity of halogen substituents in free radicals.** S. T. BOWDEN and T. F. WATKINS (J.C.S., 1940, 1242—1249, 1249—1257; cf. A., 1940, II, 302).—XI. Substitution of Me in CPh₃·OH increases the basicity of the carbinols (2:5-Me₂ > p - > o - > m -Me), and the halochromism of the sulphates, but in lesser degree than OMe. Both sulphates and neutral radicals (in C₆H₆) change colour on exposure to sunlight. The Me-substituted formates decompose more slowly than the OMe-derivatives, and the conductivity of the chlorides in liquid SO₂ is > that of CPh₃Cl (p > o > m). The rate of isomerisation of the neutral radicals to colourless products in C₆H₆ in the dark (measured photo-electrically or tintometrically) is in the order p - > m - > o -Me or 2:5-Me₂. Diphenyl-*m*-tolyl- (best prepared from Me *m*-toluate and MgPhBr), m.p. 65°, and 2:5-dimethyltriphenylcarbinol (from 2:5:1-C₆H₃Me₂·COPh and MgPhBr), m.p. 108.5° (reduced by Zn + AcOH to the -methane, m.p. 91°), with HCl in Et₂O + CaCl₂ yield the -methyl chlorides, m.p. 71° and 128.5°, respectively. The corresponding free radicals absorb O₂ in Et₂O (at about the same rate as CPh₃) giving the peroxides, m.p. 155° and 157°, respectively, together with isomeric compounds (oils), and with I gives iodides which dissociate to a greater extent than CPh₃I. Mol. wt. determinations on C₆H₆ solutions of the free radicals

show that they have a greater radical stability than CPh₃; evaporation of such solutions yields oils.

XII. p -F increases the basicity of CPh₃·OH, enhances the halochromism of its salts, and raises the decomp. temp. of the formate by 30° (the decomp. then proceeds normally). p -Fluorotriphenylcarbinol, m.p. 121—122° (from p -C₆H₄F·CO₂Et and MgPhBr), yields, via the chloride (I), m.p. 91—92°, a radical (II), m.p. 115—124°, which with O₂ yields the peroxide, m.p. 169°. On keeping in the dark, solutions of (II) change colour, and absorb less O₂ (amount decreases with time; an isomeride is formed which does not absorb O₂). Mol. Ag, when shaken with freshly prepared (II), removed part of the F giving a secondary radical, showing that this F is more reactive than that of CPh₃F. This behaviour is discussed from the viewpoint of the quinonoid hypothesis. F is also replaced by SO₄ on shaking (I) with Ag₂SO₄ in PhNO₂. Mol. wt. determinations in C₆H₆ solutions show that the unimol. stability of (II) is ~20%. A. LI.

Sterols. XCIX. Sterols from various sources. R. E. MARKER and A. C. SHABICA (J. Amer. Chem. Soc., 1940, 62, 2523—2525).—Hydrolysis (EtOH-KOH) of the EtOH extract of "Cantharides Russian" (Spanish flies) gives the urine hydrocarbon (I), m.p. 64°, β -sitosterol, and sterol carbinols, m.p. 69° (mol. wt. 256) and 201° (mol. wt. 381). Ant eggs and mare's non-pregnancy urine yield cholesterol as sole pure product pptd. by digitonin. Mexican flies yield (I) and a sterol (II), m.p. 149—151° (acetate, m.p. 130°). Chicken faeces yield sitosterol and (II). Sheep faeces yield sitostanol, (I), and a trace of carbinol, m.p. 75—79°. R. S. C.

Sterol group. XLI. New epimerisation process. (MISS) J. BARNETT, I. M. HEILBRON, E. R. H. JONES, and K. J. VERRILL (J.C.S., 1940, 1390—1393).—Al(OPr^{*i*})₃ in boiling xylene converts sterols into their epimeric forms; the yields are variable. Thus, cholesterol, lumisterol (I), neoergosterol, or cholestanol gives epicholesterol (II), m.p. 140.5°, $[\alpha]_D^{20}$ -34° in CHCl₃ (10% yield after resolution with digitonin) (benzoate, m.p. 99.5°, $[\alpha]_D^{20}$ -29° in CHCl₃), epilumisterol (III), m.p. 113° (40%) [after resolution of the racemate, m.p. 156—158°, $[\alpha]_D^{20}$ +199° in CHCl₃, of (I) + (III), with digitonin], epineoergosterol (15%), or epicholestanol (4%), respectively. The use of C₆H₆ or PhMe gives poorer yields. An equilibrium is established, as (III) and Al(OPr^{*i*})₃ in xylene (? C₆H₆) afford some (I) (as the above racemate). Ergosterol similarly in xylene gives an impure ergostatetraene, m.p. 83—93°; in C₆H₆, however, in N₂ in the dark for 160 hr., a little solid, m.p. 175—182° (? *epi*-ergosterol), separable by adsorption (Al₂O₃) into fractions, m.p. 185—190° and 173—176°, is obtained. (II) and COMe₂-Al(OBu^{*i*})₃-C₆H₆ afford 3-keto- Δ^4 -cholestene. Sublimation in high vac. (10⁻³ mm.) of ergostatienol (*epiallo*-ergosterol) (IV) or its acetate in presence of FeCl₃ (I or HgCl₂ are ineffective) gives the same hydrocarbon, m.p. 86—87°, probably (A), as obtained by Windaus *et al.* (A., 1939, II, 212). Irradiation in COMe₂ solution, or shaking with PtO₂-MeOH, has no effect on



(IV); adsorption of the acetate on alumina gives a little of a substance, m.p. 131—132° (? *epi-isoergosteryl* acetate). A. T. P.

Constitution of α -spinasterol. E. FERNHOLZ and W. L. RUGH (J. Amer. Chem. Soc., 1940, 62, 2341—2343).— α -Spinasterol (I) with O_3 in AcOH gives *d*-CHETPr ^{β} .CHO. Its benzoate with H_2 -Pd-black in Et₂O gives α -spinasteryl benzoate (II), m.p. 89°, [α]_D²⁵ +11° in CHCl₃, and thence (5% KOH-EtOH) α -spinasterol, m.p. 115°, [α]_D²⁵ +24° in CHCl₃ (acetate, m.p. 118°, [α]_D²⁵ +16° in CHCl₃), identical with α -stigmasteryl benzoate [= (II)] is obtained by reduction (as above) of 7-dehydrostigmasteryl benzoate. R. S. C.

Sterols. CI. Structure of ψ -sarsasapogenin. R. E. MARKER, E. M. JONES, and J. KRUEGER (J. Amer. Chem. Soc., 1940, 62, 2532—2536).—The formula previously assigned (cf. A., 1940, II, 171) to ψ -sarsasapogenin (I) is supported by reactions described. The composition of Δ^{16} -pregnene-3:20-dione (II) and non-identity of dihydro- ψ -sarsasapogenin (III) with dihydrosarsasapogenin (IV) are confirmed. Deoxy- ψ -sarsasapogenin (prep. from deoxy-sarsasapogenin by Ac₂O at 200° followed by hydrolysis with EtOH-KOH), m.p. 130°, and H_2 -PtO₂ in AcOH at 3 atm. give dihydrodeoxy- ψ -sarsasapogenin, m.p. 128—129°. H_2O_2 -AcOH at 70° oxidises (I) or (III) to (after hydrolysis with MeOH-KOH) a substance, C₂₇H₄₄O₅, m.p. 253—254°, and a small amount of a lactone, m.p. 282—285°. Sarsasapogenin acetate with H_2O_2 -AcOH at 70°, followed by KOH-MeOH, gives pregnane-3:16:20-triol, but bromosarsasapogenin acetate and (IV) are unaffected. KMnO₄ and (I) in ~65% AcOH at 15° give (II). O_3 converts (I) in CHCl₃ or its diacetate in AcOH into pregnen-3(β)-ol-20-one, but (III) is barely affected. Tetrahydrosarsasapogenin and Ac₂O (? at 200°) give a product, whence 5% KOH-EtOH yields tetrahydrosarsasapogenin 16-acetate, m.p. 155°. R. S. C.

Simple synthesis of α -substituted crotonic acids. H. SPIEGELBERG (Festschr. E. C. Barell [Basel], 1936, 212—216; Chem. Zentr., 1937, i, 4926).—OH·CHMe·CHR·CO₂Et (R = alkyl or aralkyl), obtained by reduction of CHRAc·CO₂Et or CHR·CAc·CO₂Et, is converted by PCl₅ into a mixture of CHMeCl·CHR·CO₂Et and CHMe·CR·CO₂Et; hydrolysis (aq. EtOH-KOH) of the mixture then gives CHMe·CR·CO₂H. Et β -hydroxy- α -benzylbutyrate, b.p. 158—160°/12 mm., from CHPh·CAc·CO₂Et by H_2 -Ni-MeOH-NHEt₂ (first at 40—60° and then at 80—90°) or from CH₂Ph·CHAc·CO₂Et by Al-Hg in moist Et₂O, thus affords α -benzylcrotonic acid, m.p. 99°. Solubility data (H₂O; Et₂O) are given for α -benzylcrotonamide, -anilide, and -benzylamide; α -*n*- and -*iso*-butylcrotonamide; α -benzyl- and α -*n*-butylcrotonylcarbamide. The amides have some hypnotic activity. H. B.

Preparation of salicylates of primary alcohols. E. LE SECH (Rev. Marques Parfum., 1937, 15, 45—46; Chem. Zentr., 1937, i, 3628).—When *o*-ONa·C₆H₄·CO₂Me is heated with CH₂Cl·CH₂·OH and a primary alcohol (ROH), group exchange occurs and

o-OH·C₆H₄·CO₂R is formed. Salicylates of sesquiterpene alcohols can thus be prepared. Santalyl salicylate has b.p. 200—235°/6 mm. H. B.

Bromo-derivatives of aromatic esters. L. ROSENTHALER (Pharm. Acta Helv., 1937, 12, 8—9; Chem. Zentr., 1937, i, 4497).—*p*-OH·C₆H₄·CO₂Me, *o*-NH₂·C₆H₄·CO₂Me, and Me anisate with Br in AcOH give Me 3:5-dibromo-4-hydroxybenzoate, m.p. 123—124°, 3:5-dibromoanthranilate, m.p. 90°, and 3-bromoanisate, m.p. 99—100°, respectively. *o*-OAc·C₆H₄·CO₂H and Br in H₂O + CaCO₃ afford 3:5-dibromoacetylsalicylic acid, m.p. 163°. H. B.

Constitution of anacardic acid, principal constituent of cashew-nut shell oil. G. D. GOKHALE, M. S. PATEL, and R. C. SHAH (Current Sci., 1940, 9, 362—363).—*n*-C₁₄H₂₉·CO₂Ph by Fries transformation yields *o*- and *p*-OH·C₆H₄·CO·C₁₄H₂₉, reduced (Clemmensen) to *o*-, m.p. 54—55°, and *p*-pentadecylphenol, m.p. 72.5°, both different from tetrahydroanacardol (I) (Smit, A., 1931, 840). Since (I) gives a Br₃-derivative and anacardol Me ether is oxidised to *m*-OMe·C₆H₄·CO₂H, (I) is *m*-OH·C₆H₄·C₁₅H₃₁, and anacardic acid is 2:6:1- or 2:4:1-OH·C₆H₃(C₁₅H₂₇)·CO₂H. A. LI.

Synthesis of iodohippuric acids. II. 2:3:5- and 3:4:5-Tri-iodohippuric acid. C. J. KLEMM and J. H. HUNTER (J. Org. Chem., 1940, 5, 508—511; cf. A., 1940, II, 277).—2:3:5:1-C₆H₂I₃·CO₂H and SOCl₂ give the chloride, m.p. 85—86° after softening at 80—84°, which with aq. NH₂·CH₂·CO₂Na followed by HCl affords 2:3:5-tri-iodohippuric acid, m.p. 255.5—257° after darkening at 250—255°. 4:3:5:1-NH₂·C₆H₂I₃·CO₂H, m.p. >350°, from *p*-NH₂·C₆H₄·CO₂H and ICl in 12.5% HCl, is converted into 3:4:5:1-C₆H₂I₃·CO₂H, m.p. 289—290°. This with SOCl₂ yields 3:4:5-tri-iodobenzoyl chloride, m.p. 138—139°, which is transformed into 3:4:5-tri-iodohippuric acid, m.p. 242—243°. H. W.

Optically active monosubstituted succinic acids and [their] derivatives. (MISS) M. NAPS and I. B. JOHNS (J. Amer. Chem. Soc., 1940, 62, 2450—2457).—Resolution of the *dl*-acid by brucine gives *d*-, m.p. 198.5—199.0°, [α]_D²⁵ +135.5° in EtOH, and *l*-anisylsuccinic acid, m.p. 196—199°, [α]_D²⁵ -122.0° in EtOH [brucine salts, 1 *d*-acid, 1 base, m.p. 197—200°, and 1 *l*-acid, 2 base, +2H₂O, m.p. 136.5—137°; anhydrides, m.p. 92.5—93.0°, [α]_D²⁵ +95.2°, [α]_D²⁰ -94.9° in EtOH, respectively; *d*-amic acid, m.p. 166—169°, [α]_D²⁵ (partly hydrolysed sample) +104.3° in EtOH (N-Me derivative, m.p. 174—175°, [α]_D²⁵ +143.0° in EtOH); *d*-anilic acid, m.p. 148—150°, [α]_D²⁵ +154.0° in EtOH; *d*-anil, m.p. 165—166°, readily racemised, [α]_D²⁵ +29.3° in C₆H₆]. *o*-C₆H₄Cl·CHO, CN·CH₂·CO₂Na, and aq. NaOH at 40° give α -cyano- β -*o*-chlorophenylacrylic acid, m.p. 208—209°, the *Et* ester (prep. by HCl-EtOH), m.p. 51—52°, of which with NaCN in 50% aq. EtOH at 100° gives the oily dicyano-ester, converted by boiling, conc. HCl into *dl*-*o*-chlorophenylsuccinic acid, m.p. 173—174° (sublimes at 167°) (anhydride, m.p. 122.0°; amic acid, softens at 156°, m.p. 164°; N-methylimide, m.p. 129—131°; anil, m.p. 143—144°). Strychnine then yields the *d*-(I), m.p. 166—168°, [α]_D²⁵ +115.0° in EtOH, and

l-acid, m.p. 166—168°, $[\alpha]_D^{25}$ -101.3° in EtOH [strychnine salts, *d*-acid, *l*-base, +2H₂O, m.p. 126—128°, and *l*-acid, *l*-base, m.p. 138°; *d*-, $[\alpha]_D^{25}$ +45.2° in EtOH, $\pm 0^\circ$ in CHCl₃, and *l*-, $[\alpha]_D^{25}$ -45.7° in EtOH, -anhydride, m.p. 145—146°; *d*-amic acid, m.p. 164—165°, $[\alpha]_D^{25}$ +19.0° in EtOH, racemises in hot H₂O (N-Me derivative, m.p. 156—158°, $[\alpha]_D^{25}$ +104.3° in EtOH); *d*-anilic acid, m.p. 169—170°, $[\alpha]_D^{25}$ +130.7° in EtOH; *d*-anil, m.p. 180—181°, $[\alpha]_D^{25}$ -27.6° in EtOH]. *d*-CO₂H·CHPh·CH₂·CO₂H (II), m.p. 173—174°, $[\alpha]_D^{25}$ +148.1° in EtOH (corresponding *l*-acid, m.p. 173°, $[\alpha]_D^{25}$ -147.8° in EtOH), gives an anhydride, m.p. 82°, $[\alpha]_D^{25}$ +99.4° in EtOH, *amic acid*, m.p. 141—145°, $[\alpha]_D^{25}$ +52.8° in EtOH, racemised and partly hydrolysed in boiling H₂O (N-Me derivative, m.p. 159—160°, partly racemised, $[\alpha]_D^{25}$ +34.8° in EtOH), *anilic acid*, m.p. 125—127°, $[\alpha]_D^{25}$ +151.8° in EtOH, and *anil*, forms, m.p. 165—166° and 140—141°. Hydrogenation (PtO₂, EtOH) of (I) or (II) gives *d*-cyclohexylsuccinic acid, m.p. 95.5—96.0°, $[\alpha]_D^{25}$ +26.3° in EtOH (*anhydride*, m.p. 43.0°, $[\alpha]_D^{25}$ +9.5° in EtOH; *anilic acid*, m.p. 172—172.5°, $[\alpha]_D^{25}$ +32.2° in EtOH; *anil*, m.p. 143.5—144.5°, $[\alpha]_D^{25}$ -41.1° in EtOH); *dl*-cyclohexylsuccinic acid, new m.p. 146°, is similarly prepared. *d*-Methylsuccinic acid, m.p. 110—111°, $[\alpha]_D^{25}$ +11.7° in H₂O [*d*-, m.p. 64—65°, $[\alpha]_D^{25}$ +32.1° in EtOH, and *l*-anhydride, $[\alpha]_D^{25}$ -32.6° in CHCl₃; *d*-, $[\alpha]_D^{25}$ +11.4° in EtOH, and *l*-, $[\alpha]_D^{25}$ -10.9° in EtOH, -*anilic acid*, m.p. 143—145°; *d*-, $[\alpha]_D^{25}$ +4.5° in EtOH or CHCl₃, and *l*-, $[\alpha]_D^{25}$ -5.5° in CHCl₃, -*anil*, m.p. 125—126°], are also described. $[\alpha]$ are given also for other λ . Ring-closure results in a marked decrease in α except for the Me derivatives. Solvent effects are noted for several of the compounds.

R. S. C.

Chemiluminescence of hydrazides of carbonylic acids. II. E. S. VASSERMAN and G. P. MIKLUCHIN (J. Gen. Chem. Russ., 1940, 10, 202—206).—The cyclic hydrazides of 4-nitronaphthalic, m.p. 336° (decomp.), of diphenic, m.p. 246° (decomp.), of 4-aminodiphenic, m.p. 140°, and of cis-1:2-dihydro-, sublimes at 270°, and cis-4:5-dihydro-phthalic acid, m.p. 253° (decomp.), have been prepared by heating the appropriate anhydrides with N₂H₄ in EtOH. Chemiluminescence is observed when H₂O₂ is added to alcoholic solutions of the hydrazides, the most intense effect being given by the two last named.

R. T.

Reactions of aldehydes with amines. I. With *o*-aminophenol. F. G. SINGLETON and C. B. POL-LARD (J. Amer. Chem. Soc., 1940, 62, 2288—2289).—*o*-NH₂·C₆H₄·OH and RCHO under any of 5 sets of conditions give *o*-, m.p. 104.5°, *m*-, m.p. 132°, and *p*-NO₂·C₆H₄·CH₂·, m.p. 161° (cf. lit.), *m*-, m.p. 105° (corr.), and *p*-C₆H₄Me·CH₂·, m.p. 108.5° (corr.), *o*-C₆H₄Cl·CH₂·, m.p. 94° (corr.), and 5:2:1-NO₂·C₆H₃Cl·CH₂·, m.p. 164° (corr.), derivatives.

R. S. C.

Addition reactions of unsaturated α -keto acids. VI. (MISS) M. REIMER and (MISS) E. TOBIN (J. Amer. Chem. Soc., 1940, 62, 2515—2520; cf. A., 1938, II, 494).—*p*-Bromobenzylidenepyruvic acid (I) (prep. from *p*-C₆H₄Br·CHO and AcCO₂H in 25% KOH-MeOH), m.p. 143° (hydrates in air) and +H₂O, m.p. 120°, and its *Me*, m.p. 122°, and *Et* ester, m.p.

77°, are sensitive to light, a dimeric *Et* ester, m.p. 167—168°, being very readily formed. H₂O₂ converts the Na salt of (I) into *p*-C₆H₄Br·CH·CH·CO₂H. Br and anhyd. (I) in dry CHCl₃ give a stable dibromide (II), m.p. 133° (decomp.), and +H₂O, softens at 100°, m.p. 120° (gas) (*Me* ester, m.p. 113°), which in boiling H₂O gives colourless β -bromo-*p*-bromobenzylidenepyruvic acid (III), m.p. 144—145° (decomp.), and +H₂O, cryst. (*Me* ester, m.p. 101°, prep. by CH₂N₂ only; *Na* salt), but in 1% Na₂CO₃ at room temp. gives a yellow isomeric acid (IV), m.p. 141—143° [*Me* ester, m.p. 75°, prep. by MeOH-HCl; with H₂O₂-Na₂CO₃ gives a bromo-*p*-bromocinnamic acid, m.p. 221° (*Me* ester, m.p. 72°)]. When heated at the m.p. or slowly in H₂O, (IV) gives (III). Dissolution in Na₂CO₃ converts (III) into (IV). (II) is accompanied by an isomeride (not obtained pure), which in 2% Na₂CO₃ gives 4: ω -dibromostyrene, m.p. 81°, oxidised by KMnO₄ to *p*-C₆H₄Br·CO₂H. (III) is probably *p*-C₆H₄Br·C $\begin{smallmatrix} \text{H} < \text{O} \\ \text{C} < \text{O} \end{smallmatrix}$ ·COH and (IV) the unchelated form.

R. S. C.

Condensations. XI. Condensations of active hydrogen compounds effected by boron trifluoride and aluminium chloride. D. S. BRESLOW and C. R. HAUSER. XII. General theory for carbon-carbon condensations effected by acidic and basic reagents. C. R. HAUSER and D. S. BRESLOW (J. Amer. Chem. Soc., 1940, 62, 2385—2388, 2389—2392; cf. A., 1940, II, 308).—XI. PhCHO with COPhMe and BF₃ gives CHPh·CH·COPh (I) (61%) and CHPh(CH₂·COPh)₂, with CH₂(CO₂Et)₂ (II) and BF₃ gives CHPh[CH(CO₂Et)₂]₂ (III) [identified as CHPh(CH₂·CO₂H)₂ (43.6%)], with (II) and AlCl₃ gives CHPh·C(CO₂Et)₂ (IV) and some (III), and with Ac₂O and BF₃ gives 4.5% of CHPh·CH·CO₂H, but it does not react with EtOAc and BF₃. (II), (IV), and BF₃ give (III), but CHPh·CH·CO₂Et and (II) do not react. (II), (I), and BF₃ probably give COPh·CH₂·CHPh·CH(CO₂Et)₂; Et₂ 2-benzoyl-1:3:5-triphenyl- Δ^1 -cyclohexene-4:4-dicarboxylate and, after hydrolysis, COPh·CH₂·CHPh·CH₂·CO₂H are isolated. 23.1% of CH₂Ph·CHAc·CO₂Et is obtained from CH₂Ac·CO₂Et, CH₂PhCl, and BF₃ at room temp.

XII. The author's theories of condensation reactions are expanded to include reactions induced by acidic catalysts. Such catalysts exert their effect on the electron-accepting component by forming an "active" co-ordination complex. CHPh·NPh, (II), and BF₃·Et₂O give 26.5% of NHPh·CHPh·CH(CO₂Et)₂. NHPh·CHPh·CHAc·CO₂Et and BF₃ in Et₂O give PhCHO and CH₂Ac·CO₂Et, and in COMe₃ give CH₂Ac·CO₂Et, NH₂Ph, and CHPh·CAc·CO₂Et. CH₂Ac·CO₂Et, Pr^{*i*}·O, and BF₃ give 70.9% of CHPr^{*i*}Ac·CO₂Et, 40.4% being similarly obtained by Pr^{*i*}OH.

R. S. C.

β -Naphthyl derivatives of ethanolamine and *N*-substituted ethanolamines. T. IMMEDIATA and A. R. DAY (J. Org. Chem., 1940, 5, 512—527).—Gradual addition of AlCl₃ to C₁₀H₈ and AcCl in cold PhNO₂ and fractionation of the product from EtOH gives a 35—40% yield of 2-acetonaphthone, m.p. 53° (picrate, m.p. 82°), converted by Br in AcOH into ω -bromo-2-acetonaphthone (I), m.p. 80° (picrate,

m.p. 93°), which with $(\text{CH}_3)_6\text{N}_4$ in CHCl_3 followed by conc. HCl gives ω -amino-2-acetonaphthone, isolated in 40–44% yield as the hydrobromide; the oxime could not be obtained. Gradual addition of NH_2Me in dry EtOH to (I) in dry Et_2O gives the unstable ω -methylamino-2-acetonaphthone (oxime, m.p. 143°), isolated as the hydrochloride in 12–15% yield. The following-2-acetonaphthones are described: ω -ethylamino-, m.p. 68° (oxime, m.p. 121°; hydrochloride, m.p. 220–222°); ω -n-butylamino-, m.p. 82° (oxime, m.p. 113°; hydrochloride, m.p. 208°); ω -benzylamino-, m.p. 84° (oxime, m.p. 116.5°; hydrochloride, m.p. 207–208°); ω -cyclohexylamino-, m.p. 125° (hydrochloride, m.p. 209–210°; oxime hydrochloride, m.p. 201–202°); ω -dimethylamino-, free base very unstable (oxime, m.p. 148°; hydrochloride, m.p. 216–217°); ω -diethylamino-, free base very unstable (oxime, m.p. 121.5°; hydrochloride, m.p. 199°); ω -dibenzylamino-, m.p. 109° (oxime, m.p. 114°; hydrochloride, sublimes without melting at 198°); ω -piperidino-, m.p. 84° (oxime, m.p. 122°; hydrochloride, m.p. 213°); ω -morpholino-, m.p. 120.5° (oxime, m.p. 154–155°; hydrochloride, m.p. 223–224°). The ketone salts are hydrogenated (10% Pd-C in EtOH) at atm. pressure thus giving the following α -2-naphthylethanol; β -amino-, m.p. 113.5° [hydrochloride (II), m.p. 186°]; β -methylamino- (III), m.p. 109° (hydrochloride, m.p. 152°); β -ethylamino- (IV), m.p. 110.5° (hydrochloride, m.p. 189.5°); β -n-butylamino- (V), m.p. 95.6° (hydrochloride, m.p. 190°); β -benzylamino- (VI), m.p. 136.5° (hydrochloride, m.p. 194.5°); β -cyclohexylamino- (VII), m.p. 98° (hydrochloride, m.p. 224°); β -dimethylamino-, (VIII), m.p. 53° (hydrochloride, m.p. 143.5°); β -diethylamino- (IX), m.p. 42° (hydrochloride, m.p. 142.5°); β -dibenzylamino- (X), m.p. 132° (hydrochloride, m.p. 210°); β -piperidino- (XI), m.p. 98.5° (hydrochloride, m.p. 213°); β -morpholino- (XII), m.p. 120.5° (hydrochloride, m.p. 223–224°). (II) is transformed by BzCl at 100° into β -amino- α -2-naphthylethyl benzoate hydrochloride, m.p. 206–206.5°; attempts to prepare the corresponding free base lead to β -benzamido- α -2-naphthylethanol, m.p. 207.8°. Similarly obtained are the benzoate hydrochloride of (III), m.p. 193–194°, and β -benzethylamido- α -2-naphthylethanol, m.p. 134.5°; benzoate hydrochloride of (IV), m.p. 178–179°, and β -benzethylamido- α -2-naphthylethanol, m.p. 125°; benzoate hydrochloride of (V), m.p. 151°, and β -benz-n-butylamido- α -2-naphthylethanol, m.p. 126–127; benzoate hydrochloride of (VI), m.p. 208°, and β -benzbenzylamido- α -2-naphthylethanol, m.p. 82°; benzoate hydrochloride of (VII), m.p. 192–193°, and β -benz-cyclohexylamido- α -2-naphthylethanol, m.p. 68°; benzoate hydrochloride of (VIII), m.p. 225°, and the base, m.p. 69°; benzoate hydrochloride of (IX), m.p. 178°, and free base, m.p. 84°; benzoate hydrochlorides of (X), (XI), and (XII), m.p. 205–206°, 209°, and 204–205°, respectively, and the corresponding bases, m.p. 111.2°, 69°, and 105°, respectively. All m.p. are corr.

H. W.

Friedel-Crafts reaction. V. Action of acetic anhydride and benzoyl chloride on methyl β -resorcyate. R. D. DESAI and (MISS) K. S. RADHA (Proc. Indian Acad. Sci., 1940, 12, A, 46–49; cf. A., 1939, II, 23).—2 : 4 : 5 : 1-($\text{OH})_2\text{C}_6\text{H}_2\text{Ac-CO}_2\text{Me}$, m.p. 124° (improved method of prep.), is converted by 1

mol. of Ac_2O into *Me* 2 : 4-dihydroxy-3 : 5-diacetylbenzoate, m.p. 113°, also obtained from *Me* β -resorcyate (I) and Ac_2O (2 mols.). The acid, m.p. 175° (*p*-nitrophenylhydrazones, m.p. >280°; semicarbazone, m.p. >280°), is transformed by HCl-AcOH at 160–170° into 2 : 4 : 1 : 3- $\text{C}_6\text{H}_2\text{Ac}(\text{OH})_2$, m.p. 95–96° (lit., m.p. 85–87°). (I), BzCl , and AlCl_3 afford *Me* 2 : 4-dihydroxy-5-benzoylbenzoate, m.p. 129–130° (2 : 4-dinitrophenylhydrazones, m.p. >270°; semicarbazone, m.p. >270°); the corresponding acid, m.p. 232–233°, is decarboxylated to 4 : 1 : 3- $\text{C}_6\text{H}_2\text{Bz}(\text{OH})_2$. *Me* 2 : 4-dihydroxy-5-benzoyl-3-acetylbenzoate, m.p. 126–127°, gives a 2 : 4-dinitrophenylhydrazones, m.p. >290°. *Me* 2 : 4-dihydroxy-3 : 5-dibenzoylbenzoate, m.p. 119–120°, is hydrolysed to the acid (+ H_2O), m.p. 235–236° (2 : 4-dinitrophenylhydrazones, m.p. >280°; semicarbazone, m.p. >290°), which is decarboxylated to 2 : 4 : 1 : 3- $\text{C}_6\text{H}_2\text{Bz}(\text{OH})_2$, m.p. 102°. H. W.

Preparation of isophorones.—See B., 1940, 782.

Cyclone series. V. S. ABRAMOV and C. L. MITROPOLITANSKAJA (J. Gen. Chem. Russ., 1940, 10, 207–209).—Cyclone (I) and $\text{CH}_2\text{:CH-CH}_2\text{:OH}$ or $\text{CH}_2\text{:CH-CH}_2\text{Cl}$ in C_6H_6 (8 hr. at 180–200°) afford 2 : 5-endoketo-2 : 3 : 4 : 5-tetraphenyl-1 : 2 : 5 : 6-tetrahydrobenzyl alcohol, m.p. 85–86°, or chloride, m.p. 115–118°, respectively. $\text{CH}_2\text{:CH-CH}_2\text{Ph}$ and (I) give 3 : 4 : 5 : 6-tetraphenyl-1 : 2-dihydrodiphenylmethane, m.p. 158–160°, whilst styrene affords 1 : 2 : 3 : 4 : 5-pentaphenyl-5 : 6-dihydrobenzene, m.p. 157–158°.

R. T.

Synthetic experiments utilising perinaphthan-7-one. L. F. FIESER and M. D. GATES, jun. (J. Amer. Chem. Soc., 1940, 62, 2335–2341).—1- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{Cl}$ [prep. from C_{10}H_8 , $(\text{CH}_3\text{O})_3$, and HCl in AcOH improved to give a 51.5% yield] and $\text{CHNa}(\text{CO}_2\text{Et})_2$ give the Et_2 ester, b.p. 167–171°/1.5–2 mm., and thence 1- $\text{C}_{10}\text{H}_7\text{-[CH}_2\text{]}_2\text{-CO}_2\text{H}$, m.p. 156–156.6° [*Me* ester, m.p. 35–36.5°; amide, m.p. 103–104° (lit., 140°, 85°, 133°)]. With AlCl_3 or SnCl_4 this gives mixtures, but in HF gives readily 81% of perinaphthan-7-one (I), m.p. 82.6–83.2° [oxime, new m.p. 127–128°; semicarbazone, m.p. 232–233° (decomp.)], with a little 4 : 5-benzhydryndone, m.p. 120.6–121.4° [oxime, m.p. 229–231° (decomp.)] (cf. Cook *et al.*, A., 1934, 519). The structure of (I) is proved by Clemmensen–Martin reduction to perinaphthane (A., 1938, II, 356). With $o\text{-C}_6\text{H}_4\text{Cl-MgBr}$, (I) gives a crude carbinol, dehydrated in boiling AcOH to mixed, rearranged anhydroderivatives, which after hydrogenation (PtO_2 ; AcOH) gives a product, b.p. 178–180°/1 mm.; interaction thereof with $\text{CuCN-MeCN-C}_5\text{H}_5\text{N}$ at 230–240° gives 1- (II) (18.6%), m.p. 144.7–145.4°, and 3-*o*-cyanophenylperinaphthane (III) (13.4%), m.p. 122.5–123.8°, and a eutectic mixture (18.3%), m.p. 104.3–106.3°, thereof. Acid hydrolysis of (II) and (III) is unsuccessful but hot KOH-aq. EtOH gives 76% of 1-*o*-carbamyl-, m.p. 173–174.5°, 17% of 1-*o*-carboxy-, (IV), m.p. 173.7–174.7°, 77.5% of 3-*o*-carbamyl-, m.p. 194.2–196.5° [hydrolysed to (V) by conc. HCl-AcOH], and 16.5% of 3-*o*-carboxy-, (V), m.p. 187.9–188.5°, -phenylperinaphthane. In HF , (V) gives 3 : 4-trimethylenebenzanthr-7-one, m.p. 217.2–218.4°, and (IV) gives 4 : 4'-trimethylene-2 : 3-benzfluorenone,

m.p. 187—189° (rapid), 201—203° (slow heating), or 190° (preheated bath) resolidifying with m.p. 201—203° (absorption spectrum resembles that of 2:3-benzfluorenone but not that of 1:2-benzanthr-10-one). M.p. are corr. R. S. C.

Constitution of the chlorobenzanthrone obtained by direct chlorination of benzanthrone. G. CHARRIER and E. GHIGI (IX Congr. int. chim. pura apl., 1934, 4, 309—316; Chem. Zentr., 1937, i, 4361—4362).—The chlorobenzanthrone, m.p. 183°, is probably the 3-derivative. Oxidation (CrO_3) gives anthraquinone-1-carboxylic acid whilst fusion with KOH affords isoviolanthrone. Oxidative fission (KMnO_4 , aq. NaOH, 85—90°) gives a *chlorodiphenyl-2(or 3):2'-dicarboxylic-3(or 2)-glyoxylic acid*, m.p. 245—250° (softens at 225°), which is converted by MnO_2 - H_2SO_4 into a substance, m.p. 237—238°, and by distillation with CaO into (probably) *p*- $\text{C}_6\text{H}_4\text{PhCl}$ and a substance, m.p. 140—160°. H. B.

Sterols. CV. Preparation of testosterone and related compounds from sarsasapogenin and diosgenin. R. E. MARKER (J. Amer. Chem. Soc., 1940, 62, 2543—2547).—*alloPregnan-20-one* and $\text{K}_2\text{S}_2\text{O}_8$ - H_2SO_4 - K_2SO_4 in AcOH at 25° give 30—35% each of 21-acetoxypregnan-20-one (I), m.p. 197—200° [semicarbazone, m.p. 242—244° (decomp.)], and 17(α)-androstanyl acetate (isolated by hydrolysis to androstan-17(α)-ol and purification of the H succinate). Hydrolysis of (I) by boiling KHCO_3 -MeOH gives *allopregnan-21-ol-20-one*, m.p. 115—117°, oxidised by CrO_3 to *ætioallocholanolic acid*. 3(α)-Acetoxypregnan-20-one and $\text{K}_2\text{S}_2\text{O}_8$ give similarly products hydrolysed to *ætiocholanolic acid*: 17(α)-diol and a little *epipregnanolone* and *ætiolithocholic acid*. 3-Acetoxy- Δ^5 -pregnen-20-one (as dibromide) gives similarly Δ^5 -androstene-3(β):17(α)-diol, m.p. 176—178°, identified by oxidation to androstene-3:17-dione. 4-Bromopregnan-3:20-dione gives products, which, after removal of HBr by $\text{C}_5\text{H}_5\text{N}$, contain deoxycorticosterone, which was hydrolysed (without isolation) by KHCO_3 -MeOH and then oxidised to 3-keto- Δ^5 -*ætiocholanolic acid*, m.p. 249—253° (reduced by Na-EtOH to 3(β)-hydroxy-*ætioallocholanolic acid*); the residual 17-acetoxy-compounds afford, after hydrolysis (1% MeOH-KOH), testosterone and progesterone. 2-Bromocholestanone, 4-bromocoprostanone, cholesterol and its acetate resist oxidation by $\text{K}_2\text{S}_2\text{O}_8$. R. S. C.

Steroids. III. Partial oxidation of 3:5:6-triols and oxidation with permanganate of 5:6-unsaturated steroids. M. EHRENSTEIN and M. T. DECKER (J. Org. Chem., 1940, 5, 544—560).—Partial oxidation ($\text{CrO}_3 = 10$) of androstane-3(β)-5:6-(trans)-triol-17-one yields *androstane-3(β):5-diol-6:17-dione*, m.p. 282—284° (3-monoacetate, m.p. 197·5—199°, $[\alpha]_D^{25} + 17\cdot0^\circ$ in COMe_2). Dehydroisoandrosterone acetate is oxidised by KMnO_4 in COMe_2 to a mixture of substances including 5:6(α)-oxido-, m.p. 188—190°, $[\alpha]_D^{25} + 58\cdot4^\circ$ in COMe_2 , and 5:6(β)-oxido- (I), m.p. 221—222·5°, $[\alpha]_D^{25} + 10^\circ$ in COMe_2 , -*androstane-3(β)-ol-17-one acetate* both of which with aq. COMe_2 - H_2SO_4 undergo ring opening to *androstane-3(β)-5:6-(trans)-triol-17-one 3-monoacetate*, m.p. 234—235°, transformed by oxidation into *androstane-3(β):5-diol-6:17-dione 3-monoacetate*, m.p. 234—235°, and by

acetylation into the 3:6-diacetate, m.p. 216·5—217°, $[\alpha]_D^{25} \pm 0^\circ$ in COMe_2 . The dehydroisoandrosterone oxide of Uschakov *et al.* (A., 1938, II, 65) and Miescher *et al.* (A., 1938, II, 174) is acetylated to (I). Oxidation (KMnO_4 in AcOH) of cholesteryl acetate gives a mixture of substances separated chromatographically into appreciable amounts of *cholestane-3(β):5-diol-6-one 3-monoacetate*, m.p. 226·5—228·5°, and *β -cholesterol oxide acetate*, m.p. 114—117°. Analogous oxidation of pregnenolone acetate affords a mixture of substances from which 5:6-oxido-pregnan-3(β)-ol-20-one acetate, m.p. 163—165° (oxime, m.p. 219—221°), *pregnan-3(β):5-diol-6:20-dione 3-monoacetate*, m.p. 222·5—224° [oxime, m.p. 262—264° (decomp.)], and a small amount of *pregnan-3(β):5:6-triol-20-one 3-monoacetate*, m.p. 226—228° (oxime, m.p. 221—223°), are isolated. The mechanism of the oxidation (KMnO_4) of 5:6-unsaturated steroids is discussed. *Androstane-3(β):5:6(cis)-triol-17-one 3:6-diacetate* has m.p. 253—254°, $[\alpha]_D^{25} + 63\cdot6^\circ$ in COMe_2 . H. W.

Sterols. CIII. Oxidation of pregnanetriols. R. E. MARKER and D. L. TURNER (J. Amer. Chem. Soc., 1940, 62, 2540—2541).—*alloPregnan-3:16:20-triol*, $\text{Al}(\text{OPr}^i)_3$, and cyclohexanone (excess) in PhMe give Δ^{16} -*allopregnene-3:20-dione*, reduced by H_2 -Pd-BaSO₄ in Et₂O at 1·7 atm. to *allopregnan-3:20-dione*. Sarsasapogenin acetate and $\text{K}_2\text{S}_2\text{O}_8$ - H_2SO_4 - K_2SO_4 in AcOH at room temp. give (after hydrolysis) *pregnan-3(β):16:20-triol*, m.p. 227—228° (lit. 223—226°), oxidised (as above) to (probably) $\Delta^{17:20}$ -*pregnene-3:16-dione*, m.p. 179—182°. R. S. C.

6-Methyl- Δ^4 -androstene-3:17-dione. O. S. MADAIEVA, M. I. USCHAKOV, and N. F. KOSCHELEVA (J. Gen. Chem. Russ., 1940, 10, 213—216).— Δ^5 -Androstene-3:17-diol and BzO_2H in CHCl_3 yield *androstene-3:17-diol 5:6-oxide*, m.p. 198—199° [*diacetate*, m.p. 165—165·5° (corr.)], which with MgMeI in Et₂O affords *6-methylandrostane-3:5:17-triol*, m.p. 117—120° (3:17-diacetate, m.p. 176·3—177·9°). This is oxidised (CrO_3 in AcOH) to *6-methylandrostane-5-ol-3:17-dione*, m.p. 187—188°, converted by HCl in CHCl_3 into *6-methyl- Δ^4 -androstene-3:17-dione*, m.p. 163·5—167°. R. T.

Preparation and properties of derivatives of inositol. F. A. HOGAN and E. BARTOW (J. Amer. Chem. Soc., 1940, 62, 2397—2400).—Prep. of inositol from [best (9·5%), light] starch steep water is modified. Oxidation to 1:2:3:5:6:4-O: $\text{C}_6(\text{OH})_4\cdot\text{O}$ (I) is best (35—40%) effected by HNO_3 (d 1·42) at room temp. The Na salt and the so-called "K rhodizionate" are salts of (I) and lead to the same products. The coloured compounds, (I), $2\text{NH}_2\text{Ar}$ (9 bases used; 6 others do not react), 22 inorg. salts of (I), and the (? tetra-)benzoate, m.p. 266—270° (decomp.), propionate, m.p. 231° (decomp.), butyrate, m.p. 237° (decomp.), isobutyrate, m.p. 121°, valerate, m.p. 241° (decomp.), isovalerate, m.p. 218° (decomp.), isohexanoate, m.p. 222—225° (decomp.), octoate, m.p. 224° (decomp.), and decoate, m.p. 208—211° (decomp.), are described. R. S. C.

1-Alkylthiolanthraquinones.—See B., 1940, 782.

Dependence of physiological action on chemical constitution. I. Difference in odour of *d*-, *l*-,

and *dl*-derivatives of amino- and diamino-methylenecamphor. B. K. SINGH and A. B. LAL (Proc. Indian Acad. Sci., 1940, **12**, A, 230—234).—The order of intensity of odour of 5- and 3-nitro-*o*-toluidino- and of 2:5- and 2:3-toluylenediamino-methylenecamphor is $l > dl > d$ in each case. Hypotheses relating odour to chemical constitution are discussed. H. W.

Dependence of optical rotatory power on chemical constitution. XVIII. Rotatory dispersion of stereoisomeric 3-nitro-*o*-toluidino-, 5-nitro-*o*-toluidino-, 2:3-toluylenediamino-, and 2:5-toluylenediamino-methylenecamphor. B. K. SINGH and A. B. LAL (Proc. Indian Acad. Sci., 1940, **12**, A, 157—178).—Hydroxymethylene-*d*-camphor in 90% EtOH and 5-nitro-*o*-toluidine in 70% AcOH at 0° afford 5-nitro-*o*-toluidinomethylene-*d*-camphor, m.p. 161—162°; the *l*- and *dl*-camphor compounds have m.p. 162° and 170°, respectively. 3-Nitro-*o*-toluidinomethylene-*d*-, *l*-, and *dl*-camphor have m.p. 98°, 98°, and 122°, respectively. 2:5-Toluylenediaminomethylene-*d*-, m.p. 215°, *l*-, m.p. 217°, and *dl*-, m.p. 136°-camphor are described. M.p. 115°, 116°, and 116° are recorded for 2:3-toluylenediaminomethylene-*d*-, *l*-, and *dl*-camphor. Rotatory powers in MeOH, COMe₂, C₆H₆, EtOH, C₅H₅N, and CHCl₃ are recorded at 35° for $\lambda = 5036, 5218, 5460, 5780, 5812, 6102, 6362, 6438, \text{ and } 6707 \text{ \AA}$. NO₂ at C₍₅₎ has a greater effect on the rotatory power than at C₍₃₎. The introduction of additional optically active centres does not result in a corresponding increase in the vals. of $[\alpha]$. The influence of Me on $[\alpha]$ is irregular. The order of $[\alpha]$ in different solvents does not run parallel with the sequence of their dielectric consts., MeOH > EtOH > COMe₂ > C₆H₅N > CHCl₃ > C₆H₆. H. W.

Kinetics of mutarotation of hydroxymethylene-*d*-camphor.—See A., 1940, I, 443.

Volatile plant substances. XII. Structure of aromadendrene. Y. R. NAVES and E. PERROTTET (Helv. Chim. Acta, 1940, **23**, 912—925).—Repeated fractional distillation of the sesquiterpenes from oil of *Eucalyptus globulus*, Labill, gives aromadendrene (I), b.p. 114°/6 mm., $\alpha_{4461} +5.96^\circ$ ($l = 1?$) hydrogenated (PtO₂) to dihydroaromadendrene (II), b.p. 104—104.5°/4 mm., $\alpha_{4461} -13.36^\circ$ ($l = 1?$), and ozonised to aromadendrone, m.p. 83.5—84°, $\alpha_{4461} +5.02^\circ$ ($l = 1?$) in EtOH. Evidence of more than one ethylenic linking has not been obtained. (I) absorbs only 1 H₂ and (II) appears saturated particularly towards C(NO₂)₄. The observation of Radcliffe *et al.* (A., 1938, II, 416) that aromadendrol is saturated towards C(NO₂)₄ and does not absorb H₂ is confirmed and it is found that oxygenated hydroazulenes are readily and completely hydrogenated. Fixation of halogens does not give any useful information probably on account of decyclisation. According to Rossmann's method (I) and (II) unite with 2.1 and 1 mol. of Br, respectively. Data are given for parachor, dispersion, dipole moment, and ultra-violet absorption and Raman spectra. H. W.

Sesquiterpenes. XLIV. Carbon skeleton of guaïol and of guaiazulene. P. A. PLATTNER and L. LEMAY (Helv. Chim. Acta, 1940, **23**, 897—907).—Hydrogenation of guaïol (*dinitrobenzoate*, m.p. 137—

137.5°) in presence of PtO₂ in cyclohexane, EtOH, EtOAc with or without AcOH, or in AcOH leads to only 33% absorption of H₂ whereas hydrogenation with Raney Ni-H₂ at 100°/100 atm. affords dihydroguaïol (I), m.p. 78—79°, $[\alpha]_D -54^\circ$ in COMe₂ (*dinitrobenzoate*, m.p. 150°, $[\alpha]_D -14.2^\circ$), and a dextrorotatory isomeride (II), $[\alpha]_D \sim +40^\circ$ (*dinitrobenzoates*, m.p. 135° and 144°). The dihydroguaïene (III) obtained from (I) and Ac₂O at 150°, AlCl₃ at 255°, BzCl in C₅H₅N followed by distillation, and KHSO₄ at 150—160° has b.p. 123—124°/11 mm., $[\alpha]_D -43.8^\circ$ in EtOH, b.p. 124°/11 mm., $[\alpha]_D -59^\circ$ in EtOH, $[\alpha]_D -57^\circ$, and b.p. 128—131°/13 mm., $[\alpha]_D -42.3^\circ$ in EtOH, respectively. Ozonisation of (III) gives notable amounts of CH₂O and COMe₂ and the product is transformed by Zn dust into a ketone, C₁₂H₂₀O, b.p. 100—120°/3 mm. [*semicarbazone* (IV), m.p. 205—206°, $[\alpha]_D -81.4^\circ$], a neutral material, C₁₅H₂₀O₂, b.p. 130—136°/3 mm., probably a mixture of the expected CO-aldehyde and a neutral peroxidic substance, C₁₅H₂₆O₃, b.p. 169°/3 mm. Prolonged keeping of the neutral products gives a cryst. substance, C₁₅H₂₆O₂, m.p. 168.5—169.5°. Similar treatment of (II) leads to a *semicarbazone*, m.p. 196—197°, $[\alpha]_D +17.5^\circ$, whilst crude dihydroguaïol affords a *semicarbazone*, m.p. 199—200°, $[\alpha]_D +46^\circ$; neither compound depresses the m.p. of (IV). Aq. H₂C₂O₄ transforms (IV) into 2:6-dimethyldicyclo-[0:3:5]-decanone, b.p. 130—131°/11 mm., $[\alpha]_D -107.4^\circ$ in EtOH, reduced (Raney Ni in EtOH at room temp.) to 2:6-dimethyldicyclo-[0:3:5]-decanol, b.p. 130—134°/10 mm. This is converted by KHSO₄ at 200° followed by S at 230° into 1:4-dimethylazulene [additive compound, m.p. 177—178°, with C₆H₃(NO₂)₃; picrate, m.p. 142—143°]. All m.p. are corr. H. W.

Triterpene resinols and related acids. XI. Oxidation of acetyloleanolic acid and of methyl acetyloleanolate with perbenzoic acid. C. W. PICARD and F. S. SPRING (J.C.S., 1940, 1387—1390).—Oxidation with BzO₂H of Me acetyloleanolate gives the oxide, m.p. 215—217° (corr.) [cf. m.p. 201—204° (corr.), Ruzicka *et al.*, A., 1937, II, 510], which with dil. HCl is isomerised to Me ketoacetyldihydrooleanolate. Similarly treatment of acetyloleanolic acid yields hydroxyacetyloleanolic acid lactone, m.p. 333°, characterised by formation of a Ac₂ derivative, and oxidation (CrO₃-AcOH) to ketoacetyloleanolic acid lactone. F. R. S.

Oxidation of lupenyl esters. E. R. H. JONES and R. J. MEAKINS (J.C.S., 1940, 1335—1339).—An examination of the absorption spectra of ketolupeol, ketolupenyl benzoate and acetate (I) (cf. Ruzicka *et al.*, A., 1939, II, 330), and ketolupenyl acetate *semicarbazone*, m.p. 251° (decomp.) [2:4-dinitrophenylhydrazones, m.p. 252° (decomp.)], has revealed that these ketones are $\alpha\beta$ -unsaturated. Ozonolysis of (I) gives CH₂O (33% yield) and the acetate-acid, m.p. 260—261°, previously obtained by Duerden *et al.* (A., 1939, II, 170), which is hydrolysed to the OH-acid, C₂₈H₄₈O₃ (*Me* ester, m.p. 220—221°, $[\alpha]_D^{20} -22^\circ$ in CHCl₃), also obtained by ozonolysis of lupenyl acetate in CHCl₃, but in AcOH an *acetate-acid*, C₃₁H₅₀O₄, m.p. 285—286° (decomp.), $[\alpha]_D^{20} -9.7^\circ$ in

CHCl_3 [Me ester, m.p. 242—245° (decomp.)], is also isolated.

F. R. S.

(A) **Abietic acid.** G. DUPONT, J. DUBOURG, and G. ROURIS. (B) **Pyroabietic acid.** G. DUPONT and J. DUBOURG (Monit. Produits chim., 1936, 18, No. 211, 8—11, 11—15; Chem. Zentr., 1937, i, 4109).—

(A) Anomalies observed in the analysis, mol. wt. determination, and amount of H_2O eliminated during heating, of abietic acid (I) are due to the presence of a small amount of H_2O of crystallisation. Crystallisation from H_2O -containing solvents gives (I), m.p. 173°, $\text{C}_{20}\text{H}_{30}\text{O}_2 + \frac{1}{2}$ or $\frac{1}{4}\text{H}_2\text{O}$, which when heated or recrystallised from anhyd. C_6H_6 , xylene, CCl_4 , or CS_2 affords anhyd. (I), m.p. 151—153°, and not abietic anhydride. This contains 1 OH (Zerevitinov) and with abs. $\text{EtOH}-\text{NH}_3$, $-\text{NaOEt}$, and $-\text{KOH}$ gives the normal NH_4 , m.p. 121—122°, Na, and K salt, respectively, which are converted into gels under the action of moisture.

(B) The final product of isomerisation (heat; acid) of resin acids is not (I), which is converted at 190—200° into dextrorotatory products. **Pyroabietic acid**, m.p. 155—159°, $[\alpha]_{5461} +54.2^\circ$, isomeric and isomorphous with (I), has been isolated from a 20 year-old resin oil and from Aleppo turpentine after heating at 250°/80 hr.

H. B.

Lignin and related compounds. L. Fractionation of acetylated cell wall constituents of red oak wood. Q. P. PENISTON, J. L. MCCARTHY, and H. HIBBERT (J. Amer. Chem. Soc., 1940, 62, 2284—2288; cf. A., 1940, II, 348).—Extraction of red oak wood meal with $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ and aq. alkali, and treatment of the product with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ at 25°, 29°, and 35° gives products, the solubility of which in CHCl_3 is 47.7, 73.3, and 78.4% (averages), respectively. Solubility thus parallels, and owes its increase to, fission of the macromols. Fractionation of the product by dioxan and CHCl_3 and pptn. from dioxan by MeOH gives products of widely differing composition. One fraction contained 87% of lignin. Sol. "carbohydrate" fractions could not be freed from OMe and probably contained combined lignin. In the natural wood the lignin, pentosans, and cellulose are probably partly but not entirely combined.

R. S. C.

Sterols. C. Diosgenin. R. E. MARKER, T. TSUKAMOTO, and D. L. TURNER (J. Amer. Chem. Soc., 1940, 62, 2525—2532).—Reactions of diosgenin (I) are interpreted in accordance with Marker's sapogenin formulæ. (I), isolated from *Dioscorea tokoro*, Makino, is stable to $\text{HCl}-\text{EtOH}$. With $\text{Al}(\text{OPr}^i)_3$ -PhMe-cyclohexanone or with $\text{Br}-\text{AcOH}$, CrO_3 , and then Zn dust, it gives Δ^4 -tigogenone (II), m.p. 186—188°, hydrogenated (Pd- BaSO_4 ; Et_2O ; 10 lb.) to isosarsasapogenone (= smilagenone), which with $\text{Al}(\text{OPr}^i)_3$ - Pr^iOH gives isosarsasapogenin (= smilagenin). Na-EtOH reduces (II) to tigogenin (oxidised by CrO_3 to tigogenone) and Ac_2O at 200° isomerises it to ψ - Δ^4 -tigogenone (III), an oil, reconverted into (II) by $\text{HCl}-\text{MeOH}$ and reduced (H_2 -Pd- BaSO_4 ; Et_2O ; 5 lb.) to ψ -sarsasapogenone. CrO_3 -AcOH oxidises (III) to Δ^4 - Δ^5 -pregnadiene-3:20-dione, m.p. 182—185°, which with Na-EtOH gives allopregnane-3(β):20(α)-diol (IV) and with H_2 -Pd- BaSO_4 gives progesterone (V) and preg-

nane-3:20-dione. With Ac_2O at 195—200°, (I) gives ψ -diosgenin (VI), forms, m.p. 190—192° and 172—174°, the oily acetate of which by Br, CrO_3 , Zn dust, and finally alkaline hydrolysis of the ketonic products gives Δ^5 - Δ^6 -pregnadien-3-ol-20-one, m.p. 212—214°. This is reduced (Na-EtOH) to Δ^5 -pregnenediol, m.p. 170—174° (and an isomeride), which is oxidised (Br, CrO_3 , Zn) to (V) and hydrogenated (PtO_2 ; Et_2O ; 3 atm.) to (IV). (VI) is reconverted by $\text{HCl}-\text{EtOH}$ into (I) and hydrogenated (PtO_2 ; AcOH; 3 atm.) to tetrahydro- ψ -diosgenin (= dihydro- ψ -tigogenin), m.p. 202—205°, obtained also similarly from ψ -tigogenin and oxidised (CrO_3) to Δ^6 -allopregnenedione.

R. S. C.

Sterols. CII. Chlorogenin. R. E. MARKER, E. M. JONES, and D. L. TURNER (J. Amer. Chem. Soc., 1940, 62, 2537—2540).—The structure of chlorogenin (I) (A., 1940, II, 99) is confirmed and the OH are shown to be at 3(β) and 6(α). Na-EtOH reduces chlorogenone (II) to (I), but H_2 - PtO_2 in EtOH at 3 atm. gives β -chlorogenin, m.p. 246—248° (diacetate, m.p. 120°; dibenzoate, m.p. 198—200°), further hydrogenated in AcOH to dihydro- β -chlorogenin, m.p. 209—210°. Cholestane-3:6-dione and Na-EtOH give the diol, m.p. 215—216°, also obtained from the 3-ol-6-one (Windaus, A., 1917, i, 265). Diosgenin and CrO_3 -AcOH give Δ^4 - Δ^5 -diosgen-3:6-dione, m.p. 194—195°, converted by Zn dust in AcOH into 6-keto-tigogenone [= (II); identity confirmed by reduction with Na-EtOH and H_2 - PtO_2]. The mother-liquors from the oxidation of crude digitogenin afford (II) and the corresponding C_{25} -epimeride (cf. Windaus, A., 1926, 409).

R. S. C.

Sterols. CVI. Sapogenins. XXXV. The supposed trillarigenin. R. E. MARKER and J. KRUEGER (J. Amer. Chem. Soc., 1940, 62, 2548—2549).—"Trillarigenin" (A., 1938, III, 837) is a $\sim 7:3$ mixture of diosgenin (I) and trillin (II), $\text{C}_{33}\text{H}_{52}\text{O}_8$, $+0.5\text{H}_2\text{O}$, m.p. 275—280° (decomp.). Vigorous hydrolysis of trillarin gives (I) and glucose; mild hydrolysis gives (II), which by vigorous hydrolysis affords (I) and glucose (identified as osazone). (II) gives a tetra-(? penta)-acetate, m.p. 202—203°, hydrolysed by 5% $\text{KOH}-\text{MeOH}$ to (II) and hydrogenated (PtO_2 ; AcOH; 70°/3 atm.) to the H_4 -acetate, which with boiling $\text{HCl}-\text{EtOH}$ affords dihydrotigogenin. Hydrogenation (PtO_2) of (II) in MeOH containing a trace of AcOH at 1 atm. gives dihydrotrillin, $+0.5\text{H}_2\text{O}$, m.p. 270°, hydrolysed to tigogenin. (II) is thus diosgenin 3-glucoside.

R. S. C.

Sclerotiorin, $\text{C}_{20}\text{H}_{20}\text{O}_5\text{Cl}$, m.p. 206—207°, metabolic product of *Penicillium sclerotiorum*, Van Beyma.—See A., 1940, III, 868.

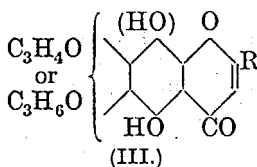
Structure of monocrotaline. IV. Monocrotalic acid. R. ADAMS and R. S. LONG (J. Amer. Chem. Soc., 1940, 62, 2289—2294).—The formula previously (A., 1940, II, 29) proposed for monocrotalic acid (I) and another considered are improbable in view of the properties of synthetic products. $\text{COMe}-\text{CHMeBr}$ and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in boiling Et_2O , PhMe, or PhMe-EtOH give Et α -carbethoxy- β -methyl-lævulate (II), b.p. 130—135°/3 mm. [2:4-dinitrophenylhydrazones, m.p. 118—119° (corr.)], hydrolysed

by boiling KOH-EtOH to α -carboxy- β -methyl-lævulic acid, m.p. 127—128° (corr.; decomp.), which at 130—140° gives CHMeAc·CH₂·CO₂H, b.p. 115—118°/3 mm. [*p*-nitrophenylhydrazone, m.p. 160—162° (corr.) (lit., 168—169°)]. The Na salt of (II) with MeI in boiling, abs. EtOH or PhMe-EtOH (less well, C₆H₆) gives *Et* α -carbethoxy- α - β -dimethyl-lævulate (III) (76%), b.p. 116—117°/2.5 mm., converted by boiling KOH-EtOH into the liquid dicarboxylic acid, which at 120° gives CHMeAc·CHMe·CO₂H (= monocrotic acid) (IV), b.p. 117—118°/3.5 mm. {Mo ester, b.p. 97—98°/20 mm. [2 : 4-dinitrophenylhydrazone, forms, m.p. 107—109° (corr.) and 121—122°, obtained also from Mo monocrotate (cf. *loc. cit.*)]}, and a little α β -trimethylangelicalactone (V). Boiling, conc. HCl converts (III) directly into (IV), but has no effect on (I). CO₂Et·CHAc·CHMe·CO₂Et, b.p. 107°/2 mm. [2 : 4-dinitrophenylhydrazone, m.p. 99—100° (corr.)], with Na and MeI in C₆H₆ or EtOH (less well, Et₂O) gives *Et* β -carbethoxy- α - β -dimethyl-lævulate, b.p. 110—115°/2 mm. {also obtained (25% yield) from CHMeAc·CO₂Et [2 : 4-dinitrophenylhydrazone, m.p. 56—57° (corr.)] and CHMeBr·CO₂Et}, which in conc. HCl at room temp. gives β -carbethoxy- α - β -dimethyl-lævulic acid (VI), b.p. 154—158°/2.5 mm., and (IV). Alkaline hydrolysis of (VI) gives (IV) and *meso*-(CHMe·CO₂H)₂; that of Me monocrotalate gives (IV) and CO₂ with a little (V). Acid hydrolysis of Me dihydroanhydromonocrotalate gives the acid, m.p. 131—132°, [α]_D²⁰ +3.80°, but alkali gives a mixture. R. S. C.

Derivatives of coumarin-3-carboxylic acid ; a new class of synthetic medicinal. F. VON WERDER (Merck's Jahresber., 1936, 50, 88—101).—o-OH·C₆H₄·CHO, CH₂(CO₂Me)₂, and a little piperidine at room temp. give *Me* coumarin-3-carboxylate, m.p. 116.5°. The following esters are prepared from the free acid (I) or the acid chloride (II): *Pr* ^{α} , m.p. 73°, *Pr* ^{β} , m.p. 89°, *Bu* ^{α} , m.p. 67°, CCl₃·CMe₂, m.p. 176°, CH₂Ph, m.p. 92°, and diethylaminoethyl (hydrochloride, m.p. 215°). The appropriate amine and (II) afford coumarin-3-carboxy-alkylamide, m.p. 130°, carbethoxyamide, m.p. 183—184° (from NH₂·CO₂Et), -ethylamide, m.p. 132—133°, -hexadecylamide, m.p. 108—110°, -phenylethylamide, m.p. 178—179°, -benzylamide, m.p. 154°, -*p*-anisidide, m.p. 215—216°, -*p*-phenetidine, m.p. 206—207°, -diethylaminoethylamide hydrochloride, m.p. 187°, -diethylamide (III), m.p. 77—78°, -dimethylamide, m.p. 144—145°, -dipropylamide, m.p. 80—81°, -diallylamide, m.p. 132°, -*di*-iso-, m.p. 137°, and -*sec*-butylamide, m.p. 148°, -diphenylamide, m.p. 236°, -*di*- β -phenylethylamide, m.p. 119—120°, -dibenzylamide, m.p. 143°, -methylpropylamide, m.p. 109—110°, -isobutyl-, m.p. 102—103°, and -isomethyl-alkylamide, m.p. 79°, -piperidine, m.p. 179—180°, -methyl-, m.p. 111—112°, and -benzyl-*p*-phenetidine, m.p. 160°, -diacetamide, m.p. 127—129°, and -*s*-diethylcarbamide, m.p. 148—149°. *Et* β -coumarin-3-carboxylamido- α -phenyl- α -methylpropionate has m.p. 111—112°. The following salts of (I) are prepared in COMe₂: dl-, m.p. 196°, and l-ephedrine, m.p. 145°, papaverine, m.p. 129°, eupaverine, m.p. 134°, quinine, m.p. 137—139°, sparteine, m.p. 157°, β -methylamino- α -*p*-aminophenylpropyl alcohol, m.p. 182°, and (?) 6 : 7-methylenedioxy-1.3' : 4'-methylenedioxyphenyl-3-methyl-

isoquinoline, m.p. 174°. 3 : 2 : 1-CH₂·CH·CH₂·C₆H₃(OH)·CHO, CH₂(CO₂Et)₂, and piperidine give *Et* 8-allylcoumarin-3-carboxylate, m.p. 88° (free acid, m.p. 147°); phenanthrocoumarin-3-carboxylic acid, m.p. 196°, is similarly obtained (as impure *Et* ester, m.p. 165°) from 3-phenanthrol-4-aldehyde. Pharmacological data are reported; (III) is a powerful sedative whilst (I) is a sedative in small and a hypnotic in large doses. CH. ABS. (b)

Derivatives of 5 : 6 : 4'- and 5 : 8 : 4'-trihydroxyflavones, and a note on the structure of ginkgetin. W. BAKER and W. H. C. SIMMONDS (J.C.S., 1940, 1370—1374).—2-Anisoyloxy-3 : 6-dimethoxyacetophenone, m.p. 131°, with NaNH₂ in PhMe gives 2-hydroxy-3 : 6 : 4'-trimethoxydibenzoylmethane, m.p. 138—139°, which with NaOAc-AcOH is finally rearranged to 5 : 8 : 4'-trimethoxyflavone (I), m.p. 161°. Partial demethylation of (I) with AlCl₃ affords the 5-OH-compound, m.p. 146° (Ac derivative, m.p. 200°). 2-Hydroxy-6-benzoyloxyacetophenone is methylated (Me₂SO₄) to the 6-benzoyloxy-2-methoxy-compound, m.p. 74°, which is hydrolysed (AcOH-HCl) to the 2-hydroxy-6-methoxy-derivative. 2-Anisoyloxy-5 : 6-dimethoxyacetophenone, m.p. 99°, is rearranged (NaNH₂-PhMe) to 2-hydroxy-5 : 6 : 4'-trimethoxydibenzoylmethane, m.p. 69°, which is further converted (AcOH-NaOAc) into 5 : 6 : 4'-trimethoxyflavone (II), m.p. 164°. Partial demethylation of (II) gives 5-hydroxy-6 : 4'-dimethoxyflavone, m.p. 173° (Ac derivative, m.p. 182.5°). Complete demethylation of (II) with AcOH-HBr yields 5 : 6 : 4'-trihydroxyflavone, m.p. 298° (Ac₃ derivative, m.p. 209°), also obtained by complete demethylation (HBr-AcOH) of (I), re-orientation of the OH groups having occurred through opening and subsequent closing of the flavone ring in the alternative direction. By comparison of properties, ginkgetin cannot be either 5 : 8- or 5 : 6-dihydroxy-4'-methoxyflavone; it is probably not a simple flavone but is best represented by (III).



F. R. S.
Structure of cannabinol. V. Second method of synthesis of cannabinol. R. ADAMS and B. R. BAKER. VI. Isomerisation of cannabidiol to tetrahydrocannabinol, a physiologically active product. Conversion of cannabidiol into cannabinol. R. ADAMS, D. C. PEASE, C. K. CAIN, and J. H. CLARK. VII. Synthesis of a tetrahydrocannabinol which possesses marihuana activity. R. ADAMS and B. R. BAKER. VIII. Position of the ethylenic linkings in cannabidiol. Marihuana activity of tetrahydrocannabinols. R. ADAMS, S. LOEWE, D. C. PEASE, C. K. CAIN, R. B. WEARN, R. B. BAKER, and H. WOLFF (J. Amer. Chem. Soc., 1940, 62, 2401, 2402—2405, 2405—2408, 2566—2567; cf. A., 1940, II, 354).—V. Olivetol, *Et* 5-methylcyclohexanone-2-carboxylate, and POCl₃ in C₆H₆ give 57% of 1-hydroxy-9-methyl-3-*n*-amyl-7 : 8 : 9 : 10-tetrahydro-6-dibenzopyrone [6''-hydroxy-5'-methyl-4''-*n*-amyl-3' : 4' : 5' : 6'-tetrahydrodibenzopyrone], m.p. 180—181° (corr.) (acetate, m.p. 82.5—84°), which with S at 255—260° gives 1-hydroxy-9-methyl-

3-*n*-amyl-6-dibenzopyrone (61%), m.p. 184—185° (corr.), and thence (MgMeI) cannabinol.

VI. Isomerisation of cannabidiol (I) to tetrahydrocannabinol, (IIa) $[\alpha]_D^{25} \sim -165^\circ$ and (IIb) $[\alpha]_D^{25} \sim -240^\circ$, is detailed (cf. *ibid.*, 355). Dehydrogenation of (II) to cannabinol and hydrogenation (PtO₂) to hexahydrocannabinol (III) are detailed. (II) and (III) have marihuana activity.

VII. Et cyclohexanone-2-carboxylate, orcinol (IV), and POCl₃ in C₆H₆ give 6''-hydroxy-4''-methyl-3':4':5':6'-tetrahydrodibenzopyrone (V), m.p. 243—245° [acetate (VI), m.p. 126—127°] (cf. Ahmad *et al.*, A., 1938, II, 198), which with MgMeI gives a product, converted by HI into 6''-hydroxy-2:2:4''-trimethyl-3':4':5':6'-tetrahydrodibenzopyrone, m.p. 136—138°. 5-Methylcyclohexane-1:3-dione, *o*-C₆H₄Br·CO₂H, and Cu(OAc)₂ give 71% of 6''-keto-4''-methyl-3':4':5':6'-tetrahydrodibenzopyrone, m.p. 148—150° (corr.), dehydrogenated by S at 255—260° to 6''-hydroxy-4''-methylidibenzopyrone (VII) (45%), m.p. 249—251° (acetate, m.p. 144—146°), obtained also (83%) similarly from (V). Dehydrogenation of (VI) causes partial hydrolysis, completion of which by HCl-EtOH yields (VII). Et 5-methylcyclohexanone-2-carboxylate, (IV), and POCl₃ in C₆H₆ give 6''-hydroxy-4''-5'-dimethyl-3':4':5':6'-tetrahydrodibenzopyrone (62%), m.p. 262—263° (Ahmad *et al.*, *loc. cit.*, 260°), which with MgMeI gives 6-hydroxy-2:2:4''-5'-tetramethyl-3':4':5':6'-tetrahydrodibenzopyran (77%), m.p. 115.5—116°. 6-Hydroxy-2:2:5'-trimethyl-4''-*n*-amyl-3':4':5':6'-tetrahydrodibenzopyran [a tetrahydrocannabinol] (VIII), b.p. 191—192°/1 mm., is similarly prepared and has marihuana activity. M.p. are corr.

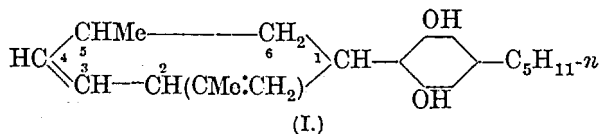
VIII. The absorption spectrum of (I) [$\log \epsilon$ 3.18; cf. $\log \epsilon$ 3.05 for (II)] and failure of (I) to react with (CH₃CO)₂O show that the ethylenic linkings in (I) are not conjugated. Differences between physical consts. of (VIII) and (II) show that neither ethylenic linking in (I) is conjugated with the aryl nucleus. Change of $[\alpha]$ of (II) [(IIa) \rightarrow (IIb)] by vigorous reagents is held to be due to migration of the endo-

oxy-2:2:4''-trimethyl-dibenzopyran, 6''-hydroxy-5'-methyl-4''-*n*-amyl-3':4':5':6'-tetrahydrodibenzopyrone, m.p. 172—173°, and 2'-hydroxy-6'-methoxy-4':3-dimethyl-6- α -hydroxyisopropyl-1:2:3:4-tetrahydrodiphenyl, m.p. 105—106°. R. S. C.

Cannabis indica. V. Synthesis of cannabinol. R. GHOSH, A. R. TODD, and S. WILKINSON (J.C.S., 1940, 1393—1396).—The Et ester, m.p. 48°, of 2':4'-dimethoxyphenyl- Δ^1 -cyclohexene-2-carboxylic acid, m.p. 153—154°, prepared from 7-hydroxy-3:4-cyclohexenocoumarin (I) and NaOH, is dehydrogenated with S, followed by demethylation (HBr) and hydrolysis to 7-hydroxy-3:4-benzocoumarin, m.p. 233°, also obtained by dehydrogenation with Pd-C of 7-acetoxy-3:4-cyclohexenocoumarin or of (I) with Se. Dehydrogenation (Pd-C) of 6''-acetoxy-2:2:4''-trimethyl-3':4':5':6'-tetrahydrodibenzopyran yields 6''-hydroxy-2:2:4''-trimethylidibenzopyran, m.p. 164°. Similar treatment of 5-acetoxy-5'-methyl-7-*n*-amyl-3:4-cyclohexenocoumarin affords 5-hydroxy-5'-methyl-7-*n*-amyl-3:4-benzocoumarin, m.p. 187° (acetate, m.p. 98°). The acetate, b.p. 140—145°/10⁻³ mm., of 6''-hydroxy-2:2:5'-trimethyl-4''-*n*-amyl-3':4':5':6'-tetrahydrodibenzopyran is similarly converted (Pd-C) into 6''-hydroxy-2:2:5'-trimethyl-4''-*n*-amylidibenzopyran, b.p. 160—165°/10⁻² mm., identical with natural cannabinol (Adams *et al.*, A., 1940, II, 354, give m.p. 75—76°). The acetate of 6-hydroxy-5'-methyl-3:4-cyclohexenocoumarin with MgMeI gives 5''-hydroxy-2:2:5'-trimethyl-3':4':5':6'-tetrahydrodibenzopyran, b.p. 130—135°/10⁻² mm., of which the acetate is dehydrogenated to 5''-hydroxy-2:2:5'-trimethylidibenzopyran. F. R. S.

Non-crystalline constituents of *Tephrosia virginiana* roots. L. D. GOODHUE and H. L. HALLER (J. Amer. Chem. Soc., 1940, 62, 2520—2522).—Roots of *T. virginiana*, L., contain 7.4% of total extractives (CHCl₃), including 2.4% of rotenone. The alkali-sol. portion of the resin yields unidentified phenols and a little tephrosin (I), dehydrorotenone, and, after "mol." distillation, a substance, m.p. 76°, insol. in alkali. Extraction of a 90% AcOH solution of the neutral portion with light petroleum removes an oil, mainly sesquiterpenes with a small amount of a drying oil. The residual neutral resin contains *l*-deguelin [racemisation by MeOH-KOH gives 20% of *dl*-deguelin (II) and hydrogenation gives *l*-dihydrodeguelin] and, after adsorption on C, further amounts of (I) and (II), with a resin, which by "mol." distillation yields a yellow substance, C₂₀H₁₈O₂(OMe)₂, m.p. 125°, α 0 in C₆H₆, and Clark's substance, C₂₀H₁₉O₃·OMe, m.p. 131°, $[\alpha]_D^{25} -95.5^\circ$ in C₆H₆. R. S. C.

Thiophen derivatives. II. N. K. CHAKRABARTY and S. K. MITRA (J.C.S., 1940, 1385—1387).—Thionation of Et β -carbethoxy- α -ethyl-lævulate gives in small yield 5-ethoxy-2-methyl-4-ethylthiophen-3-carboxylic acid, m.p. 105°; the corresponding 2:4-Me₂ compound, m.p. 125°, de-ethylated to the 5-hydroxy-2:4-dimethyl derivative, m.p. 140°, is similarly obtained. In the prep. of the following the thioketonic ester is added to emulsified Na in C₆H₆ and the α -halogenated fatty ester added: Et β -(α' -carbethoxyethylthio)crotonate, b.p. 124°/5 mm., Et α -(α' -



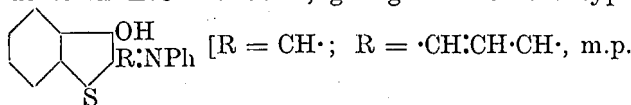
cyclic ethylenic linking, probably from the 3:4 to the 4:5 position. (I) thus has the structure shown. Relative physiological potencies are: marihuana red oil 1, (I) 0, (IIa) 2.5±0.66, (IIb) 1.75±0.25, (III) 0.70±0.10, (VIII) 0.20±0.07, synthetic hexahydrocannabinol 0.15±0.05. (IIa) and (IIb) give acetates, $[\alpha]_D^{25} -167^\circ$ and -229° , and Me ethers, $[\alpha]_D^{25} -240^\circ$ and -226° , respectively. R. S. C.

[Projected] synthesis of cannabinol. G. POWELL and T. H. BEMBRY (J. Amer. Chem. Soc., 1940, 62, 2568—2569).—Et cyclohexanone- and 5-methylcyclohexanone-2-carboxylate with orcinol or olivetol in H₂SO₄ give pyrones, converted by MgMeI into diols or tetrahydropyrans, which may be later dehydrogenated (cf. Adams *et al.*, A., 1940, II, 355). Thus are obtained 2:2:5''-trimethyl-3':4':5':6'-tetrahydro-, m.p. 69°, 2:2:5''-trimethyl-, m.p. 58°, and 6''-meth-

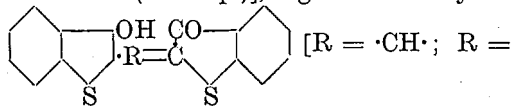
carbethoxyethylthio)ethylidenemalonate, b.p. 125°/5 mm., and *Et* β -carbethoxymethylthiocrotonate, b.p. 116°/9 mm. The action of Na on the appropriate thioether gives *Et* 3-hydroxythiophen-5-acetate (I), b.p. 96°/5 mm., and -5- α -propionate, b.p. 116°/5 mm., m.p. 53°, and *Et* 3-hydroxy-2-methylthiophen-5-acetate, b.p. 104°/5 mm. SOCl_2 and *EtI* with (I) afford respectively *Et* 3-chloro-, b.p. 128°/8 mm., and 3-ethoxy-thiophen-5-acetate, b.p. 102°/5 mm. F. R. S.

Benzene-*o*-bisthiindoxyl.—See B., 1940, 726.

Polymethine dyes of the 3-hydroxythionaphthen series. I. Condensation of 3-hydroxythionaphthen with *NN'*-diphenylformamidine and with the dianils of malonic and glutaric aldehydes. N. N. SVESCHNIKOV and I. I. LEVKOEV (J. Gen. Chem. Russ., 1940, 10, 274—280).—3-Hydroxythionaphthen and $\text{NPh}\cdot\text{CH}\cdot\text{NHPh}$ or the dianils of malonic or glutaric aldehydes condense in *EtOH* solution, giving anils of the type



217—218° (decomp.); $\text{R} = \cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot$, m.p. 201—202° (decomp.), together with dyes of the type



$\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot$, m.p. 255—257° (decomp.); $\text{R} = \cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot$, m.p. 240—242° (decomp.). The anils are readily converted into the dyes by heating with HCl-EtOH . Increase in the length of the polymethine chain shifts the absorption max. of alkaline or acid solutions of the dyes towards the red. R. T.

5-Keto-4:4-dialkyldihydropyrroles. R. ZUMBRUNN (Festschr. E. C. Barell [Basel], 1936, 206—211; Chem. Zentr., 1937, i, 4787—4788).—5-Keto-4:5-dihydropyrroles unsubstituted at $\text{C}_{4(1)}$ condense with AlkCHO and ketones in presence of bases, e.g., NH_4Et_2 ; the resulting alkylidene derivatives are reduced catalytically to the 4-alkyl derivatives, which can be obtained directly by the action of NaNH_2 and alkyl halide in boiling C_6H_6 . Mono- or di-allylation at $\text{C}_{4(1)}$ can be effected with $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ in aq. *EtOH* + Cu ; catalytic reduction then gives the *Pr* derivatives. Various *Et* 5-keto-4:4-dialkyl-4:5-dihydropyrrole-3-carboxylates have been prepared; the free acids could not be obtained by hydrolysis owing to ring fission (by acids) or non-reaction. *Et* 5-keto-1:2-dimethyl-4-ethylidene- and 5-keto-2-methyl-4-ethyl-4-diethylaminoethyl-4:5-dihydropyrrole-3-carboxylates appear new. 5-Keto-2-methyl-4:5-dihydropyrrole could not be obtained from (?) $\text{CHO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ or $(\text{OEt})_2\text{CMe}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ (I) and NH_3 . NH_2Ph and (I) give *Et* γ -anilovalerate, which could not be converted (heat; NaOEt) into a pyrrole. *Et* γ -anilovalerate does not eliminate *EtOH* at 250°; the free acid passes into 1-phenyl-5-methyl 2-pyrrolidone at <100°. H. B.

Synthesis of soporifics of the pyridine series. O. SCHNIDER (Festschr. E. C. Barell [Basel], 1936,

195—205; Chem. Zentr., 1937, i, 4642).— $\text{CET}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and HCO_2Et are condensed to $\text{OH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$, which is converted by NH_3 into $\text{NH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$ and thence (alkali) into 2:4-diketo-3:3-diethyl-1:2:3:4-tetrahydropyridine (I). This procedure is not of general applicability although the corresponding 3:3-diallyl derivative (II) can be similarly prepared; (II) is also obtained by allylation of 2:4-diketo-1:2:3:4-tetrahydropyridine in aq. *EtOH* in presence of a trace of Cu . Similar allylation of 2:4-diketo-6-methyl-1:2:3:4-tetrahydropyridine (III) [from $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (IV), $\text{CH}_2(\text{CO}_2\text{Et})_2$, and NaOEt with subsequent hydrolysis] gives its 3:3-diallyl derivative (V). The *N-Et* derivative of (III) is formed on ethylation (*EtBr*); this differs from 2:4-diketo-6-methyl-3-ethyl-1:2:3:4-tetrahydropyridine [prep. from (IV) and $\text{CH}_2(\text{CO}_2\text{Et})_2$], alkylation [other than allylation, which occurs at $\text{C}_{(3)}$] of which affords *N*-derivatives. The allyl compounds are reduced to the corresponding *Pr* derivatives. (V), which is a soporific [as is (I)], and its analogues are more strongly lipotropic than the 5:5-dialkylbarbituric acids; *N*-alkylation leads to neutral, strongly lipotropic compounds with enhanced soporific properties. H. B.

α -Pyridinium compounds of higher fatty acids.—See B., 1940, 778.

Preparation of certain quinaldine methiodides. V. A. ALEXEEVA (J. Gen. Chem. Russ., 1940, 10, 263—270).—4-Chloroquinaldine (I) and Me_2SO_4 (30 min. at -5°, 30 min. at room temp., then 20 min. at 100°) give the corresponding dimethosulphate, which with aq. KI yields 4-chloroquinaldine methiodide (II), decomp. at 222—223°. The Cl atom of (II) is highly reactive; (II) with NH_2Ph (2 hr. at 120°) gives 4-anilino-, m.p. 264° (80%), with $\text{NHPh}\cdot\text{NH}_2$ gives 4-phenylhydrazino-, m.p. 235° (97%), and with NH_2Me gives 4-methylamino-quinaldine methiodide, m.p. 290° (90%). (I) and excess of MeI (26 hr. at 100°) give 4-iodoquinaldine methiodide, m.p. 230° (decomp.) (22%). The products are conveniently analysed for halogens by Pringsheim combustion, followed by electro-titration. R. T.

Carbazolecarboxyl chlorides.—See B., 1940, 762.

Nitro- and amino-benz[f]quinolines and derivatives. W. J. CLEM and C. S. HAMILTON (J. Amer. Chem. Soc., 1940, 62, 2349—2352).—Naphth-2':1':2:3-pyridine (I) [prep. in 18.5% yield from $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, glycerol (II), H_2SO_4 , and H_2AsO_4 at 140°], m.p. 93°, with HNO_3 (d 1.5) and H_2SO_4 at -15° gives the 5'- NO_2 -compound (40%), m.p. 174°, converted by nitration at 0° into the 5':7'-(NO_2)₂-compound, m.p. 250°, which is similarly obtained from (I). 6:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$, (II), H_3BO_3 , and H_2SO_4 at 140° give 6'-nitronaphth-2':1':2:3-pyridine (34%), m.p. 240°. Hydrogenation (Raney Ni ; COMe_2 ; 2.67 atm.) of the appropriate NO_2 -compound gives 5'-, m.p. 175° (lit., 158°) (*Ac*, m.p. 235°, *CHPh*., m.p. 101°, *CH}_2\text{Ph}*, m.p. 152—154°, $\text{m-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$., m.p. 182—183°, and $\text{m-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$, m.p. 141—144°, derivative; mono- and di-hydrochloride, m.p. >300°), 6'- (III), m.p. 222—224° (dihydrochloride, m.p. >300°; *Ac*, m.p. 212—213°, and *CHPh*. derivative, m.p. 148—

151°), and 8'-aminonaphth-2': 1' : 2 : 3-pyridine (IV), m.p. 156—157° (mono- and di-hydrochloride, m.p. >300°; Ac derivative, m.p. 152—154°), and the 5' : 7'-(NH₂)₂-compound, m.p. 245—246°. The structure of (III) and (IV) is proved by oxidation to quinoline-5 : 6-dicarboxylic acid. 6-Chloro-4-methylnaphth-2' : 1' : 2 : 3-pyridine and NH₂·[CH₂]₂·OH at 180° give 6-β-hydroxyethylamino-4-methylnaphth-2' : 1' : 2 : 3-pyridine, m.p. 148—149°, which with POCl₃ at 110° gives 6-vinylamino-4-methylnaphth-2' : 1' : 2 : 3-pyridine, m.p. 163—164°. R. S. C.

5 : 5-Dianisylhydantoin.—See B., 1940, 823.

Pyrimidines. CLXV. Reaction of thiocarbamide with 5 : 5-dibromo-hydroxyhydrouracil and -barbituric acid. T. B. JOHNSON (J. Amer. Chem. Soc., 1940, **62**, 2269—2271).—5 : 5-Dibromohydroxyhydrouracil in EtOH or H₂O gives quantitatively 5-bromouracil (I) and HOBr and may thus be used as an oxidising agent. With NH₂·C(NH)·SH in EtOH or H₂O it gives (I), S, HBr, and CN·NH₂; no uracil-5-β-thiocarbamide is obtained (cf. 5 : 5-dibromobarbituric acid). R. S. C.

Synthesis of isocytosine. W. T. CALDWELL and H. B. KIME (J. Amer. Chem. Soc., 1940, **62**, 2365).—Prep. of isocytosine from guanidine hydrochloride, malic acid, and 15% oleum at <5° is described.

R. S. C.

Synthesis of compounds related to cinchonine and quinine. B. K. NANDI (Proc. Indian Acad. Sci., 1940, **12**, A, 1—19).—Et quinoline-3-carboxylate (I) and EtOAc in boiling C₆H₆ are transformed by NaOEt free from EtOH into Et 3-quinolylacetate (Cu salt, m.p. 202—203°) which could not be distilled unchanged but is converted by 25% H₂SO₄ at 100° into 3-quinolyl Me ketone (II), m.p. 98° (semicarbazone, m.p. 235°; phenylhydrazone, m.p. 202°). Passage of Br through (II) dissolved in 45% HBr at 70—75° leads to 3-quinolyl CH₂Br ketone (III), unstable, m.p. 120° [hydrobromide, m.p. 215° (decomp.)], which with piperidine in C₆H₆ at ~5° affords 3-quinolyl piperidinomethyl ketone (IV), b.p. 165—168°/15 mm. (monohydrobromide, m.p. 245—246° after becoming brown at 230°; dipicrate, m.p. 139—141°). Reduction (H₂-Pd in conc. HBr) of (IV) yields 3-β-piperidino-α-hydroxyethylquinoline, m.p. 93—94° (dipicrate, m.p. 161—163°). NHET₂ and (III) in Et₂O at room temp. give non-cryst. 3-quinolyl CH₂·NEt₂ ketone (monohydrobromide, m.p. 142—145°; dipicrate, m.p. 150—151°), which could not be distilled unchanged; it is reduced to 3-β-diethylamino-α-hydroxyethylquinoline, m.p. 89—90° (dipicrate, m.p. 139—141°). Non-cryst. 3-quinolyl CH₂·NMe₂ ketone [dihydrochloride, m.p. 157—158°; dipicrate, m.p. 147—149° (decomp.)] is reduced to 3-β-dimethylamino-α-hydroxyethylquinoline, an oil (dihydrochloride, m.p. 171—173°; Ac derivative, m.p. 139°). (I) and N-benzoylhomo-cinchonoic ester (V) are condensed by NaOEt to Et α-3-quinolyl-β-1'-benzoyl-3'-ethyl-4'-piperidylpropionate, an oil (Cu derivative, m.p. 251° after darkening at ~237°), which could not be distilled unchanged and is hydrolysed by boiling 17% HCl to β-3'-ethyl-4'-piperidyl-ethyl 3-quinolyl ketone, b.p. 225°/9 mm. (phenylhydrazone dipicrate, m.p. 195—197°). This in N-HCl and Et₂O at room temp. is transformed by dropwise addi-

tion of NaOBr into the 1'-Br-compound, m.p. 137—139°, which does not give a methiodide and is transformed by boiling NaOEt-EtOH into 3'-quinolyl 8-3-ethylquinuclidyl ketone, m.p. 122—124° (monopicrate, m.p. 167—168°); it is hydrogenated (Pd in 5% HCl) to 3'-quinolyl-8 : 3-ethylquinuclidylmethanol, m.p. 225—226° [dihydrochloride, m.p. 261—263°; platinichloride, m.p. 286—289° (decomp.)]. Et 2-methoxyquinoline-3-carboxylate (VI), EtOAc, and NaOEt in boiling C₆H₆ afford 2-methoxy-3-quinolyl Me ketone, m.p. 110—112° (phenylhydrazone, m.p. 177°). The corresponding CH₂Br ketone, m.p. 126—127°, yields the piperidinomethyl ketone, m.p. 69—71° [monohydrobromide, m.p. 251—256° (decomp.)], reduced to 2-methoxy-3-β-piperidino-α-hydroxyethylquinoline, m.p. 102—104°, the CH₂·NEt₂ ketone, m.p. 134—136°, reduced to 2-methoxy-3-β-diethylamino-α-hydroxyethylquinoline, m.p. 78—79°, and the CH₂·NMe₂ ketone (dihydrochloride, m.p. 177°), reduced to 2-methoxy-3-β-dimethylamino-α-hydroxyethylquinoline, an oil (dihydrochloride, m.p. 167—169°; dipicrate, m.p. 173—175°). (V) and (VI) yield the corresponding propionate, hydrolysed by a large excess of boiling 17% HCl to 3-ethyl-4-piperidyl 2'-methoxy-3'-quinolyl ketone, b.p. 197—200°/5 mm. (phenylhydrazone dipicrate, m.p. 188—189°). The corresponding 1-Br-ketone, m.p. 158—162°, is transformed by NaOEt in boiling EtOH into 2'-methoxy-3'-quinolyl 3-ethyl-8-quinuclidyl ketone, m.p. 155—156°, reduced to the corresponding sec. alcohol, m.p. 259—261°. The compounds are effective against paramacia but those related to cinchonine are ineffective against avian malaria; those related to quinine have not been tested. H. W.

New test for hydroxylamine by formation of "indo-oxine" [5-(8'-hydroxy-5'-quinolinyl)-imino-8-keto-5 : 8-dihydroquinoline]. R. BERG and (FRL.) E. BECKER (Ber., 1940, **73**, [B], 172—173; cf. Monti *et al.*, A., 1935, 500).—With 1% 8-hydroxyquinoline (I) in EtOH, a solution containing NH₂OH·HCl (II) (1 in 12 × 10⁶) with 2N-Na₂CO₃ gives a green coloration; at higher concns. of (II), after keeping in air, a brown Na salt of "indo-oxine" [5-(8'-hydroxy-5'-quinolinyl)imino-8-keto-5 : 8-dihydroquinoline], m.p. 253—254°, separates. This has no indophenol properties. E. W. W.

Melamine preparation. P. P. McCLELLAN (Ind. Eng. Chem., 1940, **32**, 1181—1186).—The literature of melamine (I) and related products is reviewed. (I) is now a comparatively cheap commercial product and commercial methods of prep. are compared. Solubility of (I) in H₂O is 0.5, 2.5, or 5.5% at 25°, 75°, or 90°, respectively. Pyrolysis of anhyd. CN·NH₂, guanidine (II) salts alone, or dicyanodiamidine (III) alone or in presence of solvents at atm. pressure does not give high yields of (I). Heating together (III) and (II), either dry or in presence of NH₃, improves the method. High yields of (I) are obtained by heating (II) under pressure in presence of free NH₃; some CN·NH₂, (II), and diguanide are also formed. The latter method is not improved materially by use of equimols. of CN·NH₂ and (III). The complete mechanism of the formation of (I) is not clear.

A. T. P.

Phthalocyanines.—See B., 1940, 784.

Metalloporphyrins. I. Co-ordination with nitrogenous bases. Theoretical relations. W. M. CLARK, J. F. TAYLOR, T. H. DAVIES, and C. S. VESTLING. II. Cobalt and manganese mesoporphyrins in co-ordination with nitrogenous bases. J. F. TAYLOR and W. M. CLARK. III. Co-ordination of nitrogenous bases with iron meso-, proto-, and haemato-porphyrins. T. H. DAVIES. IV. Co-ordination of iron copro- and aëtio-porphyrins with nitrogenous bases. C. S. VESTLING. V. Spectrophotometric study of pyridine [iron] coproporphyrin I. W. M. CLARK and M. E. PERKINS (J. Biol. Chem., 1940, **135**, 543—568, 569—595, 597—622, 623—641, 643—657; cf. Barron, A., 1937, III, 450).—I. A nomenclature for metalloporphyrins and their co-ordination compounds is proposed. Equations are developed for relating potentiometric and spectrophotometric data with the state of equilibrium between oxidised and reduced metalloporphyrin and the co-ordinating base.

II. The prepn. of mangani- (I), $C_{34}H_{36}O_4N_4MnOH$, and *cobalto-mesoporphyrin* (II), $C_{34}H_{36}O_4N_4Co$ [from $Co(OAc)_2$ and mesoporphyrin IX hydrochloride in glacial AcOH in absence of air], and their Me_2 esters, is described. Potentiometric titration (reduction with $Na_2S_2O_4$ in the dark or with phthiocol) of systems containing (I) or (II) and C_5H_5N , nicotine, or α -picoline shows that there is no evidence of polymerisation, that 1 equiv. per mol. is concerned in the oxidation-reduction process, and that $\Delta E_h/\Delta p_H = 0$ (E_h = electrode potential referred to H_2 standard). It appears that 2 mols. of C_5H_5N associate with 1 of mangano-mesoporphyrin, and with 1 or more of (I), and (from consideration of the Debye-Hückel simplified equation) that the net charge of nicotine Mn^{+++} -mesoporphyrin is 1, that of the Mn^{++} -compound, 2. In absence of co-ordinating base, these systems showed no stable potential. Spectroscopic measurements could not be satisfactorily interpreted. Molar extinction coeffs. for various λ s of (I) and Co^{+++} -mesoporphyrin, and log transmittance curves for Co^{+++} - and Co^{++} -mesoporphyrins in presence of nicotine, C_5H_5N , and CN' are given. No Cr mesoporphyrin could be obtained. Cu and Ni mesoporphyrins show no reversible oxidation-reduction properties.

III. Potentiometric and spectrophotometric results indicate the following. 1 equiv. per Fe is concerned in the reduction of ferri-meso-, -proto-, and -haemato-porphyrin IX in presence of nicotine, C_5H_5N , α -picoline, or CN' . Oxidant and reductant of the nicotine Fe protoporphyrin system are dimeric in H_2O , monomeric in 47% H_2O -EtOH, within the p_H range used. Other things being const., $-\Delta E_h/\Delta p_H = 0.06$ for all cases except CN' , when it is 0. Changes of E with increasing concn. of co-ordinating base show that ferro- co-ordinate better with bases than ferri-porphyrins, 2 mols. of base per Fe co-ordinating with the former, 1 or 2 with the latter. In absence of base, fluctuating potentials are observed. It is suggested that ferriporphyrins in alkaline solution are associated with 1 OH^- per Fe, and that CN^- ions compete successfully with this OH^- , neutral bases only with difficulty, if at all.

IV. The synthesis of coproporphyrin I (III) by a modification of Fischer's method is described. Spec-

troscopic measurements show that the reaction $Fe^{++} + \text{porphyrin} \rightarrow \text{ferroporphyrin} + 2H^+$ is favoured by bases, and the reverse reaction by acids; hence excess of NaOAc is used in preparing Fe porphyrins. Potentiometric titration of C_5H_5N , nicotine, and CN' complexes of Fe-(III) in buffered aq. alkali, and of C_5H_5N Fe aëtioporphyrin I (IV) in alkaline, buffered 75% H_2O -EtOH show that all species are monomeric and that 1 equiv. per mol. is involved in the oxidation-reduction. At high concns. of co-ordinating base, other things being const., $-\Delta E_h/\Delta p_H = 0.06$ for C_5H_5N (IV) or for C_5H_5N or nicotine Fe (III). 1 Mol. of ferro-(III) co-ordinates with 2 mols. of base, the dissociation consts. of these complexes increasing in the order CN' , nicotine, C_5H_5N . 1 Mol. of ferri-(III) co-ordinates with 2 mols. of cyanide, (?) mols. of other bases. The significance of the distinctive apparent dissociation consts. of C_5H_5N or nicotine ferri-(III) is discussed.

V. A photo-electric spectrophotometer is described. Photometric results confirm that 2 mols. of C_5H_5N co-ordinate concurrently with 1 mol. of ferro- or ferri-coproporphyrin. The former shows no sign of acid ionisation between p_H 8.5 and 12.4. Dissociation consts. of these complexes are given. A. LI.

Coumaronesulphonamidobenztriazoles. — See B., 1940, 824.

Synthesis and excretion of trigonelline. H. P. SARETT, W. A. PERLZWEIG, and E. D. LEVY (J. Biol. Chem., 1940, **135**, 483—485).—Trigonelline (I) hydrochloride and *H sulphate*, m.p. 199—200°, are synthesised by modifications of the methods of Winterstein *et al.* (A., 1918, i, 35). Distillation of (I) with conc. alkali gives a 96—98% yield of NH_2Me . The product of heating (I) at 75° with 6N-KOH and NH_4 salts or $CO(NH_2)_2$ gives a colour identical with that of nicotinic acid with the Bandier-Hald modification of the König reaction (A., 1939, II, 196). Normal human subjects excrete daily 1—3 mg. of nicotinic acid (II) and derivatives, 30—50 mg. of (I) (determination based on the above reaction). (II) ingested in small doses is excreted largely as (I). A. LI.

Alkaloids of Chinese drug Pai Pu. H. M. LEE and K. K. CHEN (J. Amer. Pharm. Assoc., 1940, **29**, 391—394).—The drug (*Stemona* species; total alkaloids 1.77%) contains the alkaloids *paipunine*, $C_{24}H_{37}O_4N$, m.p. 105.5—106.5°, $[\alpha]_D^{25} -53.7^\circ$ in $COMe_2$, and *sinostemonine*, $C_{21}H_{36}O_5N$, m.p. 138—138.5°, $[\alpha]_D^{25} -37^\circ$ in H_2O , the main pharmacological properties of which are described. F. O. H.

New formula for chaksine, the alkaloid of *Cassia absus*, and some experiments on its constitution. H. R. KAPUR, K. N. GAIND, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1940, **17**, 281—284).—Contrary to Siddiqui *et al.* (A., 1936, 350), chaksine is $C_{11}H_{21}O_3N_3$, not $C_{12}H_{21}ON_3$. The hydriodide, m.p. 180°, sulphate (I), m.p. 317° (decomp.), *hydrochloride* (II), m.p. 178°, *hydrobromide*, m.p. 186°, and *nitrate* (III), m.p. 220° (decomp.), are described. Addition of (III) to ice-cold H_2SO_4 leads to *nitrochaksine sulphate*, m.p. 176° (decomp.). HNO_2 transforms (II) into a nitrogenous compound, m.p. 221° (decomp.). Oxidation of (I) with H_2O_2 and $FeSO_4$ affords CH_2O . With $KMnO_4$ in alkaline

solution (I) is oxidised (KMnO_4) to $\text{H}_2\text{C}_6\text{O}_4$ and (after esterification) two *Et* esters, b.p. $80^\circ/3$ mm. and $100\text{--}105^\circ/3$ mm., respectively. H. W.

Tetra-aryl-phosphonium, -arsonium, and -stibonium salts. I. New method of preparation. J. CHATT and F. G. MANN (J.C.S., 1940, 1192—1196).— AsPh_2Cl (I) with AsCl_3 and AlCl_3 (II) at 280° gives free As, C_6H_6 and, after treatment with aq. KI, AsPh_4I (IV). When (II) is heated at $>280^\circ$ with $\text{AsCl}_3 + 3\text{C}_6\text{H}_6$, with AsPhCl_2 , with (I), with AsPh_3 or, best, with $\text{AsPh}_3 + \text{PhBr}$, followed in each case by KI, (IV) is again obtained, in varying yield. With PPh_3 at 280° , and KI, (II) gives no PPh_4I , which is, however, formed if 1 PhBr is present. SbPh_3 , 1 PhBr, and (II), followed by KBr or KI, give *tetraphenylstibonium bromide* (V), m.p. $210\text{--}218^\circ$ (according to rate of heating), or *iodide*, m.p. $\sim 200^\circ$, best obtained from (V). E. W. W.

Stereochemistry of 3-covalent arsenic. Isomeric forms of 5:10-di-*p*-tolyl-5:10-dihydroarsanthren. J. CHATT and F. G. MANN (J.C.S., 1940, 1184—1192).—Physical evidence indicates that the 3-covalent As has a pyramidal configuration with an intervalency angle of $\sim 97^\circ$.

$\text{o-C}_6\text{H}_4 \begin{smallmatrix} \text{As}(\text{C}_6\text{H}_4\text{Me}) \\ \text{As}(\text{C}_6\text{H}_4\text{Me}) \end{smallmatrix} \text{C}_6\text{H}_4\text{-o}$ should therefore be folded along the As-As axis, and should exist in two isomeric forms, a third form being impossible owing to the position of the $\text{C}_6\text{H}_4\text{Me}$ groups. Arsanthren dichloride and *p*- $\text{C}_6\text{H}_4\text{Me-MgBr}$ give α -, m.p. $178\text{--}179^\circ$, and β -5:10-di-*p*-tolyl-5:10-dihydroarsanthren, m.p. $179\text{--}181^\circ$ [no third form but a small quantity of *tri-p-tolylenediarisene* (?), m.p. $216\text{--}217^\circ$]. Both α - and β -isomerides with Br followed by aq. NH_3 give the same 5:10-di-*p*-tolyl-5:10-dihydroarsanthren *tetrahydroxide*, m.p. $\sim 318\text{--}325^\circ$ (decomp.), which is dehydrated to the *dioxide*; in the *tetrahydroxide* the C-As-C angles have become 120° and the three rings and $\text{C}_6\text{H}_4\text{Me}$ groups are co-planar. The isomerides with MeI form α - (+EtOH), m.p. $140\text{--}177^\circ$, anhyd. m.p. $176\text{--}179^\circ$ (slight efferv.), and β -5:10-di-*p*-tolyl-dihydroarsanthren *monomethiodide* (+ H_2O), m.p. $174\text{--}179^\circ$, anhyd. m.p. $176\text{--}179^\circ$. The As atoms in the ditolyl compounds show a marked reluctance to assume simultaneously the 4-covalent condition. The dimethiodide, disulphide, and monosulphide-monomethiodide could not be prepared, but a very stable *dibromide*, m.p. $298\text{--}300^\circ$ (decomp.), which probably has the quinonoid structure, and a *monosulphide*, m.p. $198\text{--}201^\circ$, have been isolated. F. R. S.

Methoxy-mercurials from *cis*- and *trans*-styryl cyanide. W. H. BROWN and G. F. WRIGHT (J. Amer. Chem. Soc., 1940, 62, 1991—1994).—*cis*- $\text{CHPh}\cdot\text{CH}\cdot\text{CN}$ reacts faster than the *trans*-isomeride with $\text{Hg}(\text{OAc})_2$ and a little HNO_3 in MeOH and gives a better yield. Equilibrium mixtures contain 99% of the product, but the second-order velocity coeffs. fall with time owing to destruction of the catalyst. The structure of the products, *cis*-, m.p. 121° , and *trans*- β -methoxy- β -phenyl- α -acetoxymercuri-propionitrile, m.p. 96° , is proved by conversion by $\text{Br}\cdot\text{CHCl}_3$ into (?) $\text{OMe}\cdot\text{CHPh}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}_2$, m.p. $219\text{--}223^\circ$, and a little $\text{OMe}\cdot\text{CHPh}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$.

R. S. C.

Catalysis in the formation of α -methoxy-mercurials from ethylenes. A. M. BIRKS and G. F. WRIGHT (J. Amer. Chem. Soc., 1940, 62, 2412—2421).—When *trans*-(CHPh) $_2$ (I) is kept with $\text{Hg}(\text{OAc})_2$ in MeOH at room temp., HgOAc is gradually pptd. (cf. A., 1935, 1515). Heating with a second equiv. of $\text{Hg}(\text{OAc})_2$ then gives 20% of $(\text{CHPh}\cdot\text{OMe})_2$. This is also formed when $\text{OMe}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{HgCl}$ from *cis*-(CHPh) $_2$ is heated with $\text{Hg}(\text{OAc})_2$. Thus failure to isolate the mercurichloride from (I) is due to the consumption thereof to give $(\text{CHPh}\cdot\text{OMe})_2$ as fast as it is formed. The accelerating action of HNO_3 in these and kindred additions is due to its peroxide content. 0.1 equiv. of Bz_2O_2 or ascaridole leads to 24% of *Hg* $\alpha\beta$ -diphenyl- β -methoxyethyl chloride, m.p. $125\text{--}126^\circ$, from (I) (BF_3 is not catalytic); reaction is slow, but after longer periods complex mixtures are formed. Peroxides initiate interaction of $\text{CHPh}\cdot\text{CH}\cdot\text{CN}$ (II) with $\text{Hg}(\text{OAc})_2$ in MeOH, but the reaction soon stops as the peroxide is destroyed; HNO_3 owes its utility in these reactions to its continuously generating small amounts of peroxide. Interaction of $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ (III) with $\text{Hg}(\text{OAc})_2$ in MeOH at 35° is accelerated by impurities in the salt and slightly by Me_2O_2 but is slightly retarded by AcO_2H , much retarded by MeCN or (II), and most retarded by $\text{C}_5\text{H}_5\text{N}$ or its acetate. Et_2S_2 also retards the reaction of (III), but itself reacts to give $\text{SEt}\cdot\text{Hg}\cdot\text{OAc}$ in equilibrium with Et_2S_2 and $\text{Hg}(\text{OAc})_2$. BF_3 accelerates the reaction of *cis*- or *trans*-(II), but simple addition is not the sole reaction. BF_3 greatly accelerates reaction of (III), but an equilibrium is set up: $(\text{III}) + \text{Hg}(\text{OAc})_2 + \text{MeOH} \rightleftharpoons \text{AcOH} + \text{OMe}\cdot\text{CHPh}\cdot\text{CH}(\text{COPh})\cdot\text{Hg}\cdot\text{OAc} \rightleftharpoons \text{Hg}[\text{CH}(\text{COPh})\cdot\text{CHPh}\cdot\text{OMe}]_2 \rightleftharpoons (\text{HgCl}_2)$. $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}(\text{COPh})\cdot\text{HgCl}$. A reaction mechanism for the catalysis is postulated. β -Methoxy- β -phenyl- α -chloromercuri-propionophenone, m.p. $150\text{--}151^\circ$, *Hg*^{II} ethylmercaptide acetate, $\text{SEt}\cdot\text{Hg}\cdot\text{OAc}$, m.p. $131\text{--}132^\circ$, a salt, $\text{C}_4\text{H}_7\text{O}_5\text{B}$, b.p. $60^\circ/8$ mm., and β -methoxy- β -phenyl- α -chloromercuri-propionitrile, m.p. 174° from *cis*-(II) and 124.5° from *trans*-(II), are described.

R. S. C.

Mercurated carvacrol. J. B. ABCEDE and A. C. SANTOS (J. Amer. Pharm. Assoc., 1940, 29, 362—364).—Carvacrol with $\text{Hg}(\text{OAc})_2$ in $\text{AcOH}\text{--}\text{EtOH}$ yields *di*(acetoxymercuri)carvacrol (I), m.p. $192\text{--}195^\circ$ (decomp.); the reaction products treated with saturated aq. NaCl afford *di*(chloromercuri)carvacrol, decomp. $216\text{--}218^\circ$ (cf. Burt, A., 1936, 619). (I) with 10% aq. NaOH gives the Na salt (?), decomp. 180° , and, when subsequently treated with CO_2 , the *oxide*, decomp. $223\text{--}250^\circ$, of *di*(hydroxymercuri)carvacrol.

F. O. H.

Interconversion reactions of organolithium compounds. H. GILMAN, W. LANGHAM, and F. W. MOORE (J. Amer. Chem. Soc., 1940, 62, 2327—2335).—General principles of metallation and halogen-Li interconversion are discussed. Prep. and manipulation of organo-Li compounds are improved. The amounts of ArCO_2H obtained from PhBr, PhI, *m*- $\text{C}_6\text{H}_4\text{ClI}$, *p*- $\text{C}_6\text{H}_4\text{ClBr}$, *p*- $\text{C}_6\text{H}_4\text{Br}_2$, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeBr}$, *p*- $\text{C}_6\text{H}_4\text{MeI}$, *p*- $\text{C}_6\text{H}_4\text{PhBr}$, *o*- and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OMe}$, and *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{OMe}$, usually in petroleum ether or Et_2O , under varying conditions are reported.

1:3:5- $C_6H_3Br_3$ gives $LiC_6H_3Br_2$. Replacement of one and partly of two Br occurs with 1:2:5- $C_6H_3MeBr_2$, $p-C_6H_4Br_2$, $(p-C_6H_4Br)_2$, 2:4:6:1- $C_6H_2Br_3OMe$, and $(p-C_6H_4Br)_2O$. In light petroleum at room temp. $CHPh:CHBr$ and $LiBu^a$ give $CHPh:CHBu^a$ and $(CHPh:CH)_2$, but, if boiled, give 23% of $CHPh:CHLi$ (with CO_2 gives *trans*- $CHPh:CHCO_2H$); in Et_2O 42.5% of $CPh:CLi$ [gives $(CPh:C-CO_2H)$] is obtained. R. S. C.

Relative reactivities of organometallic compounds. XXXII. Indium triphenyl. H. GILMAN and R. G. JONES (J. Amer. Chem. Soc., 1940, 62, 2353—2357; cf. A., 1940, II, 316).—The order of increasing reactivity is $InPh_3 > GaPh_3 > TlPh_3$. In general, increasing activity parallels decreasing ionisation potentials of the metals. $InPh_3$ (prepared in 65—81% yield from $HgPh_2$ and In in N_2 at 130°), m.p. 208° (lit., 291°), oxidises and hydrolyses rapidly in air, does not react with Hg in boiling C_6H_6 , and gives the Michler ketone colour reaction anomalously only if used in excess. With O_2 in C_6H_6 it gives ~17% of $PhOH$ and 20% of Ph_2 . It reacts slowly with CO_2 , giving after 4 hr. in boiling xylene 18% of $BzOH$. With 1 mol. of $PhCHO$ in boiling C_6H_6 it gives 82% of $CHPh_2OH$ with $InPh_2I$ and $InPhI_2$, but with 0.3 mol. gives 20% of $PhCHO$; equilibrium occurs thus: $InPhI_2 \rightleftharpoons InPh_2I + InI_3$ and $InPh_2I \rightleftharpoons InPh_3 + InI_3$, both $InPhI_2$ and $InPh_2I$ yielding $CHPh_2OH$ by interaction with $PhCHO$. With $CHPh_2CH_2COPh$ it gives only (92%) $CHPh_2CH_2COPh$. All the Ph radicals react with $BzCl$: in C_6H_6 40% and in petroleum ether 31% of $COPh_2$ is obtained; $InPh_2I$ in $CHCl_3$ gives 70% of $COPh_2$. With $COPh_2$ in boiling xylene it gives 58% of CPh_2OH . It does not react with $EtOBz$ or $PhCN$. R. S. C.

Carboxylic acids of phthaloyl-thionaphthen and -selenophen.—See B., 1940, 727.

Diphenyl series. IV. Diphenyl derivatives of phosphorus, arsenic, and antimony. D. E. WORRALL (J. Amer. Chem. Soc., 1940, 62, 2514—2515; cf. A., 1930, 1195).— $o-C_6H_4PhCl$ (I), PCl_3 , Na , and a trace of $SbCl_3$ in boiling C_6H_6 give *tri-o-diphenylphosphine*, m.p. 151 — 152° after softening [oxide (prep. by Br or Cl_2 , followed by $KOH-EtOH$), m.p. 184 — 185° ; *methiodide*, m.p. $>250^\circ$ (decomp.), with Ag_2O gives Ph_2]. $AsCl_3$, (I), and Na in boiling C_6H_6 give *tri-o-diphenylarsine*, m.p. 190° [*dihydroxide*, m.p. 237 — 238° ; *methiodide*, m.p. $\sim 154^\circ$ (decomp.), with Cl_2 gives the iodochloride, m.p. 172 — 174° (decomp.)]. Use of $SbCl_3$ gives similarly *tri-o-diphenylstibine*, m.p. 208 — 209° [*dibromide*, m.p. 152 — 154° ; *dichloride*, m.p. 174 — 175° ; *dihydroxide*, m.p. 243 — 244°], which with $SbCl_3$ in xylene at 220 — 250° gives *mono-o-diphenylstibine hydroxychloride*, m.p. 201 — 202° , converted by NH_3-EtOH into the *oxide*, m.p. 195 — 196° , and by Cl_2-H_2O into *diphenylstibinic acid*, m.p. $\gg 300^\circ$. R. S. C.

Relative reactivities of organometallic compounds. XXXIV. Thallium phenyl. H. GILMAN and R. G. JONES (J. Amer. Chem. Soc., 1940, 62, 2357—2361).—Reactions of *Tl triphenyl* in boiling xylene are interpreted as due to pyrolysis to Ph_2 and reactive $TlPh$, much Tl being also formed. $TlPh_3$,

prepared from $TlPh_2Br$ and $LiPh$ in warm xylene, has m.p. 169 — 170° (N_2 ; softens at 167° ; decomp. 180 — 185°). In boiling xylene, $TlPh_3$ and CO_2 give 70% of $BzOH$ and 73% of Ph_2 ; possibility of this reaction proceeding by way of *TlPh₂ benzoate* (prep. from $TlPh_3$ and $BzOH$ in boiling C_6H_6), m.p. 259 — 260° , is excluded by the stability thereof in boiling xylene. $TlPh_3$ with $COPh_2$ in boiling xylene gives a little CPh_2OH and with $PhCN$ a little $COPh_2$, with Ph_2 in both cases, but it does not react with $EtOBz$. $TlCl$ reacts with $LiPh$ at -70° , probably to form $TlPh$; Tl and Ph_2 are the products isolated. $TlPh_2Br$ does not react with $BzCl$ in boiling C_6H_6 or $PhMe$. With Na in liquid NH_3 , $TlPh_2Br$ gives $TlPh_3$, $NaBr$, and Tl , the $TlPh_3$ being isolated by conversion into $TlPh_2OBz$. $LiBu^a$ and $TlPh_3$ give a solution whence CO_2 yields 66% of $BzOH$. $AgBr$ and $MgEtBr$ in Et_2O at 0° give $AgEt$, which decomposes spontaneously to give 48% of C_4H_{10} and 3.5% of C_2H_4 . R. S. C.

Hydrolysis of ovalbumin in presence of acids and salts at various temperatures. I. Time of hydrolysis in autoclave and acid hydrolysis of autoclave hydrolysates. II. Effect of acids, salts, and temperature on hydrolysis in autoclave. A. B. SILAEV (Kolloid. Shurn., 1938, 4, 593—602, 603—609).—I. In the initial stages of hydrolysis in an autoclave there is rapid formation of NH_3 . As heating proceeds, the hydrolytic fission of the protein almost ceases, but deamination of the products, possibly both intermediate and final products, continues rapidly. Examination of the acid hydrolysis of the autoclave hydrolysate suggests that the mechanism of deamination is different in these two types of hydrolysis.

II. Prolonged hydrolysis with 2% H_2SO_4 in an autoclave at 180° does not effect complete resolution of the protein into NH_2 -acids, but concurrent with the hydrolysis there is deamination of the NH_2 -acids, which is not retarded by increase of $[H_2SO_4]$, or much affected by the presence of salts or H_3BO_3 . Rise in temp. from 150° to 180° for 3 hr. hydrolysis doubles the rate of hydrolysis and the rate of deamination. Deamination is largely to be ascribed to pyrolysis, at the autoclave temp., of relatively unstable NH_2 -acids formed at the beginning of hydrolysis. R. C.

Volatile aldehydes liberated by periodic acid from protein hydrolysates. A. J. P. MARTIN and R. L. M. SYNGE (Nature, 1940, 146, 491—492).— HIO_4 in aq. $NaHCO_3$ rapidly liberates $MeCHO$ from threonine. Serine, alanine, cystine, tyrosine, arginine, etc. gave no volatile aldehyde. After hydrolysis (HCl), wool, casein, and gelatin yield $MeCHO$, and wheat gluten $MeCHO$ and $EtCHO$ with HIO_4 - $NaHCO_3$; β -hydroxynorvaline may thus be present in the gluten hydrolysate. L. S. T.

Analysis of proteins. XII. Dephosphocaseose or depocaseose. T. J. R. MACARA and R. H. A. PLIMMER (Biochem. J., 1940, 34, 1431—1448; cf. A., 1939, II, 294).—The prep. of depocasein (I) and depocaseose (II) by the action of 1% $NaOH$ at 37° for 24 hr. on caseinogen (III) is described, and the amounts of the individual NH_2 -acids in (I)

and (II) are determined. (I) and (II) have low P content and both contain less N than does (III), whilst (II) contains slightly more N and S than does (I). (II) contains less arginine, tyrosine, and glutamic acid, and more lysine and methionine, than does (III), whilst (I) contains more arginine, tyrosine, and glutamic acid, and less lysine, histidine, and methionine, than does (III). Both (I) and (II) contain less threonine and β -hydroxyamino-acids than (III), but more are present in (II) than in (I). Assuming that 1 mol. of cystine is present for each mol. of (I) and (II), the mol. wt. of the latter are 80,000 and 100,000, respectively. It is concluded that 1% NaOH scarcely affects the peptide linkings in (III), but hydrolyses the ester linkings by which H_3PO_4 is bound and approx. half of the dicarboxylic acid amide groups, and separates the complex system of (III) into the two main components (I) and (II), which may or may not be homogeneous. J. N. A.

Preparation of Nessler's reagent.—See A., 1940, I, 444.

Apparatus for determination of sulphur by the evolution method.—See A., 1940, I, 446.

Microchemical technique. IV. Micro-determination of mercury and halogen in organo-mercuric halides. G. O. STONESTREET and G. F. WRIGHT (Canad. J. Res., 1940, 18, B, 246—251).—Br and Cl are determined by heating with $Ag_2Cr_2O_7$ — $K_2Cr_2O_7$ —conc. H_2SO_4 in O_2 (Zacherl *et al.*, A., 1932, 709), and Hg in the residue by titration with dithizone (Winkler, B., 1936, 168). In some cases further heating with fuming HNO_3 — H_2SO_4 is necessary to complete the decomp. A. Li.

Quantitative analysis of mixtures of polyethylene glycols by fractional distillation. S. PERRY and H. HIBBERT (J. Amer. Chem. Soc., 1940, 62, 2561—2562).—Such analysis is accurate (96—99.8%). R. S. C.

Ketoses. XVIII. Van Slyke procedure for determination of β -hydroxybutyric acid. H. BLUNDEN, L. F. HALLMAN, M. G. MOREHOUSE, and H. J. DEUEL, jun. (J. Biol. Chem., 1940, 135, 757—759).—Experiments on the Van Slyke method with pure Ca Zn *l*- and *dl*- β -hydroxybutyrate, and with the Et *dl*- β -ester containing traces of $CH_3Ac \cdot CO_2Et$, give vals. for the wt. of Hg ppt. equiv. to 1 g. of β -hydroxybutyrate of 9.51, 9.68, and 9.62, respectively. A. Li.

Determination of benzoic acid. R. W. SUTTON and O. HITCHEN (Analyst, 1940, 65, 502).—Unless the air oven described by Monier-Williams (B., 1927, 502) is copied in full detail, either a higher temp. (180°) or a longer time of sublimation than specified by him may be required for the quant. sublimation of BzOH. J. W. S.

Micro-methods for determination of sphingomyelin and choline.—See A., 1940, III, 946.

Chemical determination of thiamin by a modification of Melnick-Field method.—See A., 1940, III, 818.

Determination of morpholine. I. S. SHUPPE (J. Assoc. Off. Agric. Chem., 1940, 23, 824—831).—

Pptn. and colour tests for morpholine (I) are described and titration data given. With CS_2 (I) yields *morpholine morpholyldithiocarbamate*, sublimes at $>100^\circ$; reduced by $K_3Fe(CN)_6$ to a thiuram disulphide (?), m.p. 150—151°. The prep. of *benzene*-, m.p. 119°, and *p*-*bromobenzene-sulphonyl-morpholine*, m.p. 153°, is described. Methods of determining (I) in creams and ointments, based on steam-distillation and titration with acid and on quant. conversion into the above derivatives, are described. F. O. H.

Identification of traces of barbituric acid by a modification of the Parri reaction. E. SELLÉS (Anal. Fis. Quím., 1940, 36, 115—118).— 2×10^{-6} g. of a 0.01% solution of barbituric acid in Et_2O or EtOH may be detected by micro-technique on addition of a drop of the solution to paper saturated with 1% $Co(NO_3)_3$ in EtOH followed by a drop of 5—10% aq. NH_3 added at the edge of the paper. F. R. G.

Micro-crystallographical detection of uric acid. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1937, 75, 73—78; Chem. Zentr., 1937, i, 4833).—Uric acid deposited on acidification of an alkaline solution, or on addition of H_2O to a conc. H_2SO_4 solution followed by washing with H_2O , gives characteristic crystals after ~5 min. A. J. E. W.

Microchemistry of xanthine. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1937, 75, 79—80; Chem. Zentr., 1937, i, 4833).—Xanthine separates as characteristic crystals on dilution of its conc. H_2SO_4 solution. A. J. E. W.

Quantitative characteristics of nicotine colour reaction with cyanogen bromide and β -naphthylamine. L. N. MARKWOOD (J. Assoc. Off. Agric. Chem., 1940, 23, 792—800; cf. B., 1939, 1171).—The optimum p_H for the reaction is ~10; neutralisation to phenolphthalein is recommended. When alkaline solutions of nicotine (I) are neutralised with AcOH, HCl, or H_2SO_4 , sensitivity is greatest with AcOH and least with HCl. NaCl and, to a greater extent, Na_2SO_4 have a desensitising effect. Conditions for max. development of colour [which, for concns. of (I) >8 mg.-%, follows Beer's law] are described. F. O. H.

Turbidimetric determination of nicotine as phosphotungstate. L. N. MARKWOOD (J. Assoc. Off. Agric. Chem., 1940, 23, 800—804).—Nicotine (1—6 μ g. per ml.) is determined by photometric measurement of the turbidity produced by phosphotungstic acid in presence of dil. H_2SO_4 . F. O. H.

Micro-chemical tests for alkaloids. C. K. GLYCART (J. Assoc. Off. Agric. Chem., 1940, 23, 746—747).—Eserine is detected by PbI_2 reagent and stovaine by the characteristic crystal picture given by $AuCl_3$ reagent in presence of conc. HCl. F. O. H.

Nature of the Feulgen reaction with nucleic acid. H. N. BARBER and J. R. PRICE (Nature, 1940, 146, 335).—The effect of C_5H_5N and piperidine (A., 1940, II, 319) is not equiv. chemically to the Feulgen reaction, but is due to their basicity. Three of the purines used by Semmens (*loc. cit.*) gave no colour reaction. The Feulgen reaction is regarded as sp. for the potential $\cdot CHO$ of chromatin. L. S. T.